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Evaluation of DOM Coagulation Kinetics and Potential Process Impacts

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Evaluation of DOM Coagulation Kinetics and Potential Process Impacts

By

Eli Baer Townsend

A thesis submitted to the

Faculty of the Graduate School of the University of Colorado at Boulder in partial fulfillment of the requirement for the degree of Master's of Science

Department of Civil, Environmental, Architectural Engineering

Committee Chair: Professor R. Scott Summers

This thesis entitled:

Evaluation of DOM Coagulation Kinetics and Potential Process Impacts

Written by Eli Baer Townsend
Has been approved for the Department of Civil, Environmental, Architectural Engineering

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Dr. R. Scott Summers

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Dr. JoAnn Silverstein

Date_____________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Abstract

Townsend, Eli B. (M.S., Civil Engineering, Department of Civil, Environmental, Architectural Engineering)

Evaluation of DOM Coagulation Kinetics and Potential Process Impacts

Thesis directed by Professor R. Scott Summers

Coagulation is a commonly used treatment practice for drinking water applications. Traditionally, coagulation has been used for particle removal. However, with the emergence of disinfection byproduct (DBP) regulations, which are formed through a reaction between dissolved organic matter (DOM) and the disinfectant chlorine, coagulation is also used to remove of DOM, to inhibit the formation of DBPs. Research has been published exploring the kinetics of particle formation during coagulation, but there is little to no published research examining DOM coagulation kinetics.

Three treatment approaches that are commonly carried out around the coagulation process and may be impacted by DOM coagulation kinetics are: (1) the use of powdered activated carbon (PAC) to remove seasonal taste and odor (T&O) compounds [2-methylisoborgeol (MIB) or geosmin], (2) direct filtration where conventional sedimentation is omitted, and (3) disinfection with chlorine. These treatment processes could be further optimized if DOM coagulation kinetics were known.

DOM kinetic coagulation experiments were performed on eight surface waters with a range of water quality parameters. It was found that DOM coagulation occurs within the first ten to twenty seconds of the coagulation process. Temperature, pH, rapid mix mixing speed, turbidity, coagulant type, and coagulant dose had no effect on the kinetics of coagulation in the range evaluated.

Use of PAC, direct filtration, and chlorination were examined after DOM coagulation had occurred. PAC was less effective after DOM coagulation, while chlorination formed fewer DBPs when applied after DOM coagulation. Direct filtration demonstrated little to no carryover of DOM through filtration once DOM coagulation occurred.

PAC addition was further investigated as traditionally PAC was added at the rapid mixing stage. PAC was added at four different contact times prior to coagulation, simultaneously with a coagulant, and at two different addition times after coagulation. It was found that PAC worked most effectively in removing MIB when applied prior to coagulation. Earlier addition times of PAC provide more removal of MIB, but would also require large reactors with associated capital costs. The ten-minute addition time prior to coagulation was chosen as the most efficient location for PAC addition to remove MIB.

Acknowledgments

It takes a village….

Dr. Fernando Rosario-Ortiz was one of the first professors to invest his faith in me and support me through tough times. His kindness, generosity, oversight, and wisdom have tremendously impacted my life and the way in which I think. His research group as whole, including Simón Mostafa, Caitlin Glover, Mandi Hohner, and Kaelin Cawley, was the perfect place for me to get my feet wet in academic research.

Dr. JoAnn Silverstein was also of the utmost importance in my professional development and education. It was in her class that I first realized my ability and potential for engineering solutions. Numerous times a week I would go to her office and just talk about life, engineering, politics, etc. Without her I would not be half the man I am today, and I most definitely would not have been able to achieve the research goals presented herein.

Dr. R. Scott Summers has continued to have a profound impact on my professional development. See, Scott was both by undergraduate and graduate advisor, and, I had a tough freshman year. I didn't go to class, I didn't do homework, and I just didn't care. I spent that summer in between freshman and sophomore year in deep reflection. When I returned to school after summer concluded, I looked him in the eye and told him that I was going to be one of his graduate students one day. His response was one I will never forget: "Show me, it will be an uphill battle." He was right, it was.

When I reached the goal of joining his research group, I immediately began to rely on other members of the group: Kyle Shimabuku, Anthony Kennedy, Dave Kempisty, Julie

Korak, Tyler Dougherty, and last, but absolutely not least, Leigh Gilmore. I would not have been able to do half of the things that I did without these people. Not one of them.

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I also would be negligent if I did not thank my parents, David and Regina, and my sister, Margaret, for all of their support. Weather it was calming me down when I would get worked up over meaningless issues, or simply got excited about my studies, they were and will continue to be there for whatever I need. An ear to listen, a voice to calm, they know how to finely tune their son and brother.

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Introduction

1.1 Drinking Water Treatment Needs

Drinking water utilities are obligated to provide safe, clean, clear water to customers at all times. Water is a human right, fundamental to everyday needs and vital to survival. While there are a wide range of regulated contaminants, requiring treatment and removal from drinking water supplies, unregulated contaminants can contribute more nuisance and require higher costs when evaluating treatment options. Unregulated contaminants can cause aesthetic issues and can be in the form of foul taste, odd odor, and/or discoloration of water.

Drinking water contaminants are regulated in two categories: primary contaminants and secondary contaminants. Primary contaminants require treatment to concentrations lower than mandated a maximum contaminant level (MCL), or, in impaired water, undergo treatment via a mandated treatment technology (TT). Secondary contaminants have non-enforceable guidelines, but can cause aesthetic issues and typically result in a large number of customer complaints.

Primary contaminants are sectioned into six major categories: microorganisms, disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals, and radionuclides. Each drinking water agency or utility experiences different levels of these contaminants. A diverse set of treatment processes have been developed to address these issues; some treatment processes can address multiple concerns. While primary contaminants must be removed from drinking water prior to distribution, secondary contaminants are removed as needed and can often result in higher operational costs associated with treatment.

Taste and odor (T&O) compounds are nuisance contaminants as they are not regulated and can result in a large number of customer complaints. T&O are linked together due to the way smell and taste are experienced by people. T&O can come from various sources, such as hydrogen sulfide, improper disinfection, and algal (cyanobacteria) metabolites. Cyanobacteria excrete metabolites in high concentrations resulting in episodic “spikes” that occur throughout the year. During episodic spikes of T&O, additional treatment is required to maintain water that is aesthetically pleasing (Hepplewhite, et. al., 2004).

Powdered activated carbon (PAC) is a widely used treatment technology to control episodic T&O spikes. One challenge when applying PAC is homogenizing it in water and PAC is generally added as a slurry mixture. In lieu of the mixing challenges associated with PAC application, one conventional practice is to add PAC during the rapid mix process of a coagulation process, at the same time coagulants are added. Coagulants are required in surface water treatment to control particles (turbidity), and dissolved organic matter (DOM) as it reacts with chlorine to form disinfection byproduct (DBP). Very little research has been published to demonstrate where in a treatment process the best point of PAC addition is for T&O control.

Since PAC is applied prior to sedimentation and filtration, the maximum contact time of PAC with the water ranges from 0.5 to 1.5 hours. Longer contact times of PAC are required to adequately treat aesthetic issues and meet consumer needs. However, there is not a standard practice or a guideline set for the application of PAC.

The work presented herein is meant to address the uncertainty over where the best point of PAC addition is within a conventional drinking water treatment process to remove T&O, specifically targeting locations in the coagulation process. The target organic contaminants in this study are DOM, measured as dissolved organic carbon (DOC), and a select T&O compound, 2-methylisoborneol (MIB). Previous research on this topic focuses solely on MIB as T&O is of primary concern when PAC is applied. Previous research has concluded that DOM can foul PAC, reducing the capacity for T&O removal.

Chapter 2
Background

2.1 PAC Removal of MIB

Seasonal algal blooms can cause spikes in T&O compounds MIB and geosmin. MIB and geosmin are not effectively removed by conventional drinking water treatment and, therefore, require additional processes for removal. This presents a problem for drinking water utilities experiencing these issues, because conventional drinking water treatment is not effective at removing T&O and utilities are forced incur higher capital and operating costs for satisfactory T&O removal. T&O compounds are generally non-toxic, but they are detectable at very low concentrations ~10 ng/L (Zoschke, et al. 2011). Generally, MIB can be detected at a lower concentration that geosmin. **Error! Reference source not found.** displays the structure of MIB.

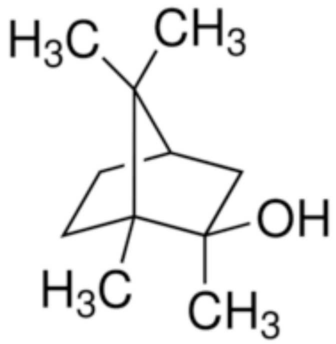

Figure 2.1: Chemical structure of MIB.

MIB is an aliphatic tertiary alcohol with a molecular weight of 168.28 g/mol and is considered to be spherical in shape with a diameter of 0.6 nm. It is miscible in water as demonstrated by a solubility over 300 mg/L, but it has a relatively high octonal-water partitioning coefficient ($LogK_{ow}$) of 3.31. Aliphatic alcohols have a reported range of -0.7

to 3.7 (Schwarzenbach, et. al., 2003) MIB is a volatile compound when there is a large enough concentration in solution.

Weishaar, et al. (2003) discussed specific ultra-violet absorbance (SUVA) to be used as a corollary for determining the coagulability of source waters. SUVA, is calculated as ratio of ultraviolet absorbance (UVA) to DOC. SUVA values below 2 $L*mg\text{-}C^{-1}*m^{-1}$ are not easily coagulated. SUVA is also correlated with aromaticity because aromatic moieties strongly absorb UV light. Therefore, aromatic compounds are more readily coagulated while aliphatic compounds are harder to coagulate. T&O compounds are often aliphatic and are not easily removed by chemical reactions, such as coagulation.

One treatment technique used to remove T&O is adsorption by PAC. Kristiana, et al. (2011) evaluated the use of enhanced coagulation coupled with PAC to remove DBP precursors at full scale. While the main focus of this study was to evaluate the reduction of DBPs both in the plant and in the distribution system, insight can still be gained. Kristiana, et al. (2011) reported that reduction of natural organic matter (NOM) increased when using high doses of PAC (~80 to 100 mg/L) that are unlikely to be used in any U.S. treatment plant. They did note, however, that while NOM decreased 70%, the DBP formation was reduced to a greater capacity, near 95% reduction. This is one of the few studies that does not focus on NOM removal when using PAC with coagulants, instead of MIB removal. It is important to consider what changes occur to the complete water matrix when using any treatment process, i.e., PAC or coagulation, not just focusing on removal of one compound.

The character of NOM can have a significant influence on the adsorption of MIB via PAC (Newcombe, 1994). Typically, PAC is applied at the same point or time when coagulants are added. This is because conventional plant operation is to add the two at the same time. There already exists a rapid mix process at the beginning of flocculation to evenly disperse coagulants; adding PAC during this point is simple from an operational standpoint.

Cho (1996) developed two models for the prediction of both MIB and DOC removal from raw surface waters, based on influent DOC, contact time, and PAC dose. This research also examined the adsorption affinity for MIB by PAC, both in the presence and absence of coagulants (ferric) and demonstrated that in the presence of coagulants, MIB adsorption onto PAC was typically decreased. However, the data showed inconsistent results where, in some cases, the capacity was increased while, in others, it was decreased. These models are presented below in Equations 1 and 2.

(1)

$$\frac{[MIB]}{[MIB]_0} = \beta_0 + \beta_1 {*}[DOC]_0 + \beta_2 {*}[Dose] + \beta_3 {*}[time]$$

(2)

$$[DOC] = \beta_0 + \beta_1 {*}[DOC]_0 + \beta_2 {*}[Dose] + \beta_3 {*}[time]$$

In Equation 1, the fraction of MIB remaining, not removed, is the dependent variable. In Equation 2, the equilibrium DOC concentration at a specified time is the dependent variable. The beta values are all empirical constants that depend on the PAC type.

Cho (1996) developed these models using three different PAC types, bituminous-based PAC, lignite-based PAC, and wood-based PAC. As each of these PAC types have a different absorptive capacity, dictated by the surface chemistry of the PAC, no one consistent set of parameters can be used. The first two beta values are positive, indicating that a higher influent DOC concentration results in more MIB and DOC remaining in solution. This is indicative of competition between DOC and MIB for removal due to PAC. The third and fourth beta value are both negative, indicating that a longer contact time, or a higher PAC dose, will result in less DOC and MIB remaining in solution, or enhanced removal.

The influence coagulants have on the adsorption of DOC was not incorporated into these models. If the initial DOC is important for determining the equilibrium concentrations of both DOC and MIB, and coagulation can remove upwards of 50% of the DOC, then why would the influence of coagulation not be included? PAC is added simultaneously as coagulants; it would be insightful to incorporate the ability of water to be coagulated such as SUVA, pH, or turbidity.

Longer contact times are required to provide adequate removal of target compounds, such as MIB, by PAC. When PAC is added in absence of coagulants, research has demonstrated that NOM can compete in two ways, either by pore blocking or direct competition. The latter of these mechanisms is due to the small size fraction, while the former is a result of larger organics reaching the carbon surface first, blocking a wide range of pores and channels within and on the carbon (Hepplewhite, et al., 2004). While both the large and small size fractions can compete with the MIB for adsorption onto PAC, the smaller size fractions are more responsible for the competitive nature of the bulk organics (Shimabuku, et al., 2014).

If coagulation removes aromatic organics, as indicated by the influence of SUVA on DOM coagulation, and both the small and large organics can compete with MIB, then it would be logical that after coagulation competition between DOC and MIB would be lessened, and more MIB removal would be observed. Cho's model has the influent DOC as an influencing factor for MIB adsorption. Therefore, it is important to evaluate how quickly DOC is tied up in by the floc structure and subsequently removed. For example, standard coagulation/flocculation/sedimentation processes consist of one stage of rapid mix followed by two to five stages of flocculation followed by sedimentation. If the organics are tied up in the floc structure by the first, or second stage of flocculation then PAC may be added at this point.

2.2 Coagulation

The original use of coagulation followed by flocculation and sedimentation was for particle control. However, a focus on DOM removal began when it was recognized that DOM was a DBP precursor. Standard practice is to preform coagulation response curves that are used to determine the optimal dose of coagulant to reach low turbidities (<2 NTU) and meet the Environmental Protection Agency (EPA) mandated removal based on influent alkalinity (mg-$CaCO_3$/L) and total organic carbon (TOC). Table 2.1 presents the EPA mandated TOC removal requirements which were developed based on coagulation of DOM.

Table 2.1: EPA TOC removal requirements.

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0 to 60	>60 to 120	>120
>2.0 - 4.0	35%	25%	15%
>4.0 - 8.0	45%	35%	25%
>8.0	50%	40%	30%

Higher TOC concentrations are harder to coagulate because organic molecules directly impact the coagulant demand of source waters. The required removal percent is also based on alkalinity because as alkalinity increases, it is more difficult for coagulants to lower the pH to a point where charge neutralization and destabilization of particles and DOM occur.

Edwards (1997) developed a model to predict equilibrium DOC concentrations after coagulation, based on equilibrium pH, initial DOC, and influent SUVA. In this model, as the pH increases there is less removal of DOC; similarly, when the initial DOC increases, the same phenomenon occurs. SUVA has the inverse effect: as higher SUVA values exist; more DOC will be removed. This is due to the efficiency of coagulation depending on the reactivity (SUVA) of the DOM. There are some limitations within this model. Firstly, there is no term that includes particle concentrations or turbidity of a source water. Edwards (1997) developed this model using source waters with turbidities below 9 NTU. When additional waters were examined to validate the model, waters with higher than 9 NTU displayed the largest deviations and were consistently found to have almost 20% error, under-predicting the amount of DOC removed. One reason for this is because particles provide nucleation sites for coagulation flocs to form. As the flocs grow larger, the absorptive capacity for dissolved organics can increase.

In addition to the lack of turbidity data included within Edwards model, there is no term within the model incorporating the mixing time or mixing speed. At lower mixing speeds, advective forces are diminished, and dispersive forces become more dominant. The mixing or flocculation time may also be an important factor when determining the equilibrium DOC concentrations, especially when attempting to investigate where PAC should be added. When flocculation proceeds for long times the flocs grow in size and gain a large enough mass to settle out quickly during a sedimentation process. However, this does not explain how fast the DOM is tied up in the floc structure.

Hussain, et al. (2013) examined the flocculation index on a kinetic basis to determine how quickly the growth of floc particles occurs. In this study they evaluated two different source waters, both with SUVA values above 2 $L*mg\text{-}C^{-1}*m^{-1}$. They did not examine how hard-to-coagulate waters react kinetically, or, more specifically, how DOM is removed based on time. This research is insightful for predicting how quickly the particles will settle after coagulation, but not the degree of removal of DOM. If the EPA has a mandated removal requirement for DOC then it would be much more useful to examine the kinetics of DOC removal through a coagulation process, not just how quickly the flocs grow. This approach is more practical and can provide better information for both utility operators and researchers.

While there has been little research published regarding how quickly DOC reaches equilibrium in a coagulation process, Arias and Summers (2014) explored how coagulation of organic matter influences DBP formation and removal. In this work, upon chlorination, halogenated organic matter (HOM) concentrations were evaluated prior to coagulation, during coagulation, and after filtration post coagulation. It was found that as more and more organic matter had been removed from solution, i.e., more treatment, the DBP yields were lower and lower. If the speed of the DOC-coagulant reaction could be assed then an earlier time of chlorination may be viable. Chlorinating earlier in a plant would allow for utilities to meet the EPA mandated CT (concentration*time) disinfection criteria at lower chlorine doses.

The main point of coagulation is to grow flocs to the point where they will settle over time and reduce the turbidity, so kinetic investigation of turbidity is not as meaningful as other parameters. Measuring DOC kinetically is much easier to do than either pH or turbidity. Samples can be taken from batch systems and filtered through vacuum filters in a few seconds. This allows for adequate representation of the DOC in the system, as any of the organic molecules that were too small to be retained on the filter are now large enough to be held up and removed from solution.

2.3 Overall Research Objectives

- Evaluate coagulation kinetics for DOM removal
- Evaluate the impact of DOM coagulation kinetics on other drinking water treatment processes

2.4 Significance of Research

This research can be used by drinking water utilities and future researchers to further evaluate practices involving PAC use for T&O control. It has the potential to help treatment plant operators reduce the PAC use rate to increase T&O removal. This will also provide a better understanding of the coagulation-PAC nexus and help to determine if there is any positive or negative effect when using both treatment processes in unison or staged.

Chapter 3
Materials

3.1 PAC

The PAC used for all experiments was a WPH, manufactured by Calgon Carbon. This form of PAC originates from bituminous coal and has moisture content of 8% (maximum). Calgon Carbon states that 99% of the PAC has passed through a #200 Mesh Sieve (diameter (d) = 0.074 mm), 95% through a #100 Mesh Sieve (d = 0.149 mm) and 90% through a #325 Mesh Sieve (d = 0.044 mm). In the subsequent sections the carbon will be referred to as bituminous based and simply PAC.

3.2 Coagulant

The alum used was hydrated aluminum sulfate ($Al_2(SO_4)_3*18H_2O$) produced Fisher Scientific. The ferric used was hexahydrate ferric chloride ($FeCl_3*6H_2O$) also produced by Fisher Scientific.

3.3 Source Waters

Eight different surface waters, one wastewater effluent, and two fractionated waters were used in these experiments. Surface waters in this study come from a variety of sources as indicated in Table 3.1. BC1 and BC2 are both waters sampled from Boulder Creek, but at different locations and at different times. The three waters labeled DW are all taken from the same drinking water reservoir, but at different times and different conditions. FCB stands for Fort Collins Baseline water and was sourced from the Poudre River just west of Fort Collins, CO. GLR is from a reservoir in Loveland, CO and stands for Greeley-Loveland Reservoir. This water has the most anthropogenic inputs of any of the surface waters. B.res stands for Boulder Reservoir. >1K and <1K

BEM are fractionated waters taken from a surface water called Big Elks Meadow. BEM was initially high in DOC (~12 mg-C/L) but during fractionation and concentration, even higher DOC values were reached. Aliquots of the size fractions were spiked into dechlorinated tap water to attempt to recreate the background inorganic matrix seen in the raw surface water. Water quality parameters for both size fractions are for the spiked-diluted product water. BWW is the one wastewater effluent studied in this research. It was taken from the outfall of the City of Boulder's 75th St wastewater treatment plant, prior to the effluent blending with the natural stream. The last water studied in this research is CUP which stands for the University of Colorado Pond by the campus' engineering center.

Table 3.1: Abbreviations and locations for source water.

Name	Location	Abbreviation
Boulder Creek #1	Boulder Creek at Ebben G. Fine Park May ‘14	BC1
Denver Water #3	Ralston Reservoir April '14	DW3
Fort Collins Baseline	Cache la Poudre River April ‘14	FCB
Denver Water #2	Ralston Reservoir Dec '13	DW2
Greely-Loveland Reservoir	Greeley Reservoir Early-June '14	GLR
Boulder Creek #2	Boulder Creek at 28th St. Bridge June '14	BC2
Boulder Reservoir	Boulder Reservoir Mid-June '14	B.Res
Big Elks Meadow Large Size Fraction	Big Elks Meadow, Fractionated June '12	>1K BEM
Big Elks Meadow Small Size Fraction	Big Elks Meadow, Fractionated June '12	<1K BEM
Denver Water #4	Ralston Reservoir September '14	DW4
Boulder Wastewater	Boulder 75th St. Treatment Plant Late-Sept. '14	BWW
University of Colorado Pond	Holding pond on University of Colorado at Boulder main campus June '14	CUP

3.4 2-Methylisoborneol

MIB is a nonionic compound. Log K_{ow} is 3.31 for MIB and it has a MW of 168 g/mol. ^{14}C MIB was obtained from American Radiolabeled Chemicals, Inc. (St. Louis, MO) and diluted with the respective cold compound (Sigmga Alrich, (St. Louis, MO)) to yield specific activities of 55 mCi/mmol. MIB activity was detected using liquid scintillation counting and had detection limits near 10 ng/L with a confidence level of 95% (Shimabuku, et al., 2014).

Chapter 4
Methods

4.1 Organic Carbon

TOC and DOC concentrations were measured in accordance with Method 5310 C (Standard Methods, 1998). For DOC, samples were collected and immediately filtered through a 0.45 µm membrane filters (Pall Life Sciences). Filters were rinsed with at least 250 mL of reverse osmosis water to minimize carbon leaching from the filter. If the samples were not measured the same day as generation, then they were stored at 4°C. All TOC or DOC analysis was performed within three days of sample collection. Analysis utilized a Sievers 5310 C Laboratory Total Organic Carbon Analyzer and the DataPro 5310 C soft was subsequently used to process the data. Samples were analyzed in groups of three or four with a blank in between to assure that operation was stable and there was no organic carbon carryover from previous samples. The instrument was calibrated in accordance with the Operations & Maintenance manual that accompanied the instrument upon installation. Quality assurance and quality control “test runs” were performed on a monthly basis to assure that drift over time was minimal.

4.2 UV_{254nm} Absorbance

Ultra-violet absorbance at 254 nm (UVA_{254}) was measured using a DR/4000 Spectrophotometer produced by HACH. Samples were analyzed using a 1-cm quartz cell and absorbance values were reported with units of cm^{-1} as spectral absorbance coefficients. Samples were taken directly out of the same vials that were run on the Sievers TOC Analyzer. UV analysis was preformed within a week of sample collection.

Samples were periodically tested at larger intervals to assure that the samples were stable and the UV reported is representative. If samples were not measured the same day as collection, then they were stored at 4°C.

4.3 Turbidity

Turbidity was measured in accordance with Method 2130 B (Standard Methods, 1998) using a 2100N Turbidimeter (HACH Company). Turbidity measurements are reported as nephlometric turbidity units (NTU) and were measured on whole, unfiltered water. Measurement vials were stored dry at room temperature and pre rinsed with de-ionized water and dried before use to assure no dilution of samples.

4.4 pH

pH was measured using a Denver Instruments, model 220 pH probe. The pH probe was calibrated weekly with pH values of 4, 7, and 10. This range of pH allows for the full range of values that are expected throughout the tests. Measurements were made by directly inserting the probe into each batch system immediately after sedimentation.

4.5 DBP Formation Tests and Analysis

THM, HAA5, and HAN concentrations were carried out in accordance with EPA Method 551.1 while for HAAs EPA Method 552.2 was used. 60 mL sample vials were rinsed with deionized water and muffled at 550 °C for 3 hours. Prior to sample collection, 6 mg of ammonium chloride was added to the vials to quench the formation of DBPs upon sample collection. Samples were analyzed within one-week of collection on an Agilent 8890 series gas chromatograph (GC).

4.6 Fluorescence Measurements

A Hobriba FluoroMax-4 (Irvine, CA) fluorometer was run in S/R (signal/reference) mode using excitation and emission bandwidths of 5 nm and integration times of 0.25 s to collect fluorescence excitation and emission matrixes (EEMs). Lamp, Raman, and cuvette checks were completed at the start of each day to ensure reliable performance. Excitations went from 240 to 450 nm at 10 nm increments and emissions went from 300 to 600 nm using 2 nm increments. EEMs were corrected by blank subtraction, Raman normalization, instrument specific corrections, and inner filter corrections using UV spectra gathered with a Cary 100 Bio UV-vis spectrophotometer (Palo Alto, CA). The fluorescence index (FI), which is the ratio of emission intensities at 520 nm and 470 nm with an excitation of 370 nm (Korak, et al., 2015).

4.7 2-methylisoborneol

Samples were collected and filtered through a 0.45 μm filter and subsequently diluted with 4 mL of sample and 16 mL of Liquid Scintillation Cocktail (UltimaGold) from PerkinElmer. 2-methylisoborneol was measured using a Tri-Carb Liquid Scintillation counter, from PerkinElmer. MIB activity was detected using liquid scintillation counting and had detection limits near 10 ng/L with a confidence level of 95% (Shimabuku, et al., 2014).

4.8 Size Fractionation

The two size fractions investigated were isolated by a fractionation/concentration method where a recirculating tangential flow ultrafilter membrane with a molecular weight cutoff of 1,000 Daltons was utilized (Amicon regenerated cellulose 1 kDa cartridge). The molecular size stock of less than 1,000 Daltons was at a concentration of 21 mg-C/L and greater than 1,000 Daltons stock was at a concentration of 120 mg-C/L (Shimabuku, et al., 2014).

4.9 Batch Experiments (Jar Tests)

Batch experiments were performed using a jar test apparatus (Phipps & Bird) that allows for set mixing times at specific mixing speeds. Standard jar test experiments for coagulation involve adding coagulants at different concentrations in different jars and varying the mixing speed and time to simulate the rapid mix, flocculation and sedimentation processes. The jar tester apparatus used automatically changed mixing speeds and held constant speed for a set time. For all tests, the rapid mix regime was for one minute at 290 rotations per minute (rpm). The rapid mix was followed by two distinct flocculation stages both for ten minutes. The first mixing regime was set for 55 rpm while the second was set for 25 rpm. Following the dual flocculation stages there was a thirty-minute sedimentation period. This procedure will be referred to as the standard jar test protocol (SJTP), and the entire test lasts fifty-one minutes. Immediately after sedimentation, samples were collected using syringes and filtered through a 0.45 µm membrane filter (Pall Life Sciences). Rectangular containers (Phipps & Bird) with a capacity of 2 liters were used.

In the coagulant alone and PAC alone experiments, the alum or PAC addition was at the beginning of the test. For the coagulation followed by PAC experiments, the jar tests were run under the conditions specified above with 2 liters of water and, after the sedimentation phase, water was decanted and dosed with PAC under the same mixing conditions. These tests were performed for an additional 51 minutes and subsequently sampled and filtered immediately after the second sedimentation period.

In the delayed chlorination experiments a slightly amended STJP was used. In these tests chlorine was added simultaneously with the alum and one minute after alum (immediately after the rapid mix). At this point the water is still moving close to the high rotational speed of rapid mix to provide good mixing for chlorine.

In experiments where temperature was varied and held constant during the jar test, temperature was monitored over the entire 51-minute jar test. In the low temperature case, water was stored in a freezer at 4 °C for 3 hours. The test jar was fitted with a thermometer. The test started with water at 9 °C and finished with water at 11 °C so an average of 10 °C was assumed. Similarly, at 30 °C a thermometer was used to monitor drift, starting at 31 °C and ending at 29 °C. In the high temperature case, a hot water bath was used to raise the temperature by 10 °C.

4.10 Error

The error associated with these experiments was calculated by performing about 20% of the jar tests in duplicate and sampling in duplicate for some of the sample points. The error used is the maximum operational plus analytical error observed across all jar tests. For DOC measurements, this is 6.5% (n=15), and for MIB measurements this is 5.8% (n=8).

Chapter 5
Coagulation Kinetics

5.1 Introduction

5.1.1 Background

Dissolved organic matter (DOM) is a primary concern in drinking water treatment, as many DOM fractions react with chlorine to form disinfection byproducts (DBPs), which may have adverse health effects. Two groups of organic DBPs are currently regulated in the US: total trihalomethanes (TTHMs) and the sum of five haloacetic acids (HAA5). DOM concentrations can vary seasonally in surface waters (Boeckman and Joeseph 2007). As a result of seasonal variations, robust treatment strategies are required to provide high quality drinking water.

DOM is comprised of a mixture of organic molecules stemming from a variety of sources. DOM can be naturally occurring or anthropogenic and may be derived from plant, algal, or human matter. The differences in DOM source, and quality, can impact drinking water treatment process efficiencies.

One of the primary processes for DOM removal is coagulation followed by sedimentation, where DOM sorption onto metal-hydroxide (floc) particles or co-precipitation with floc particles occurs (Water Quality and Treatment: A Handbook of Community Water Supplies 1990). Hydroxide complexes are created quickly, but the creation of the solid floc particle ($Me(OH)_x$ (s)), required for sorption, takes longer than other hydroxide complexes (Amirtharajah & Mills, 1982). If sorption onto floc particles is the primary mechanism for DOM removal during coagulation, then there would be a time delay to create the necessary floc particles required for sorption.

Co-precipitation occurs when charged metal hydroxide complexes react with partially charged DOM. Partially charged DOM is soluble in water and this process renders it insoluble and may occur quickly, as demonstrated by the rapid pH decrease upon coagulation. When the coagulant reacts to form a hydroxide, protons are left in solution and the pH drops. Generally, in surface waters with higher particle concentrations the coagulant demand is higher. A higher coagulant demand results in lower pH. At pH ranges where metal hydroxide still carries a positive charge, charge neutralization can occur. At higher pH ranges, metal hydroxide complexes carry a neutral charge and would result in coprecipitation. Therefore, when turbidities are higher, and more coagulant is needed, charge neutralization is more likely to occur (Water Quality and Treatment: A Handbook of Community Water Supplies 1990). Once sorption of DOM occurs, removal by subsequent processes, such as sedimentation or filtration becomes efficient.

Standard practice is to perform laboratory based coagulation dose response tests (jar tests) to determine the optimal coagulant dose required to reach target turbidities. In addition, jar tests can be used to find the coagulant dose required to meet the U.S. Environmental Protection Agency (EPA) guidelines for total organic carbon (TOC) removal prior to primary disinfection.

The coagulation process for removing DOM is based on several water parameters. Coagulant dose is important, as it provides the cation for charge neutralization, or at higher does, it forms amorphous hydroxide floc particles. It also consumes hydroxide ions and can lower the pH. Alkalinity is important, as it determines the buffering capacity of the water and to what level pH depression will occur. As source water alkalinity increases it is more difficult for coagulants to lower the pH to a point where charge neutralization can occur. pH also plays an important role in DOM coagulation. As source water pH increases, there is a higher coagulant demand by the system, requiring a higher coagulant dose to reach desired pH ranges for charge neutralization. The equilibrium pH during coagulation determines the level of protonation of DOM molecules and can influence the destabilization of DOM (Amirtharajah & Mills, 1982).

Specific UV absorbance (SUVA) is defined as the ultraviolet (UV) absorbance, measured at 254 nm, divided by the dissolved organic carbon (DOC)*100 of a water. SUVA is directly correlated with the efficiency of DOM coagulation (Weishaar, et al., 2003). Higher SUVA values correspond with a higher level of DOM aromaticity. Aromaticity is indicative of a higher electron density, and electron rich structures can experience a larger number of reaction pathways. Lower SUVA values indicate that there are more aliphatic, or branched structures, which are less reactive (Weishaar, et al., 2003).

There is a lack of practical theory and applied knowledge within the research community regarding kinetic removal of DOM during coagulation. Literature discussing kinetics of coagulation is primarily focused on modeling growth of coagulant flocs and the incorporation of particles (turbidity) into the floc structure. There is little practical information on kinetic DOM removal. The approach of Yang, et al. (2013) combines Smoluchowski's model of floc growth with fractal theory. Smoluchowski's model is a differential model that incorporates the rate of floc-particle growth and particle removal in one equation. Fractal theory presents the concept of fractal dimensions of the flocs with the particle-floc-geometry due to their largely porous structure and large light scattering potential. This theory dictates that a higher fractal dimension corresponds to flocs that have a much lower porosity, but higher density (Yang, et al., 2013). This research is related to the growth of floc structures and not the removal of DOM by coagulation.

Hussain, et al. (2013) examined the flocculation index on a kinetic basis to determine how quickly the growth of floc particles occurs. This research demonstrated that the initial growth of the flocs can occur during the first three minutes of coagulation. Residence times in flocculation can be as high as thirty minutes and often occur in a segmented, tapered array (Water Treatment: Principles and Design 2012). Hussain, et al., (2013) did not examine how DOM is removed over time. Even though the flocs have grown, there is no evidence that the DOM has been removed. Understanding how quickly DOM is tied up in the floc structure can be valuable to drinking water utilities if they have a problem with DBP formation within their treatment process or distribution system.

Arias and Summers (2003) showed that the DOM, measured by DOC was removed after three minutes of rapid mixing and additional samples taken throughout the jar test presented no additional DOC removal. However, TOC removal was not achieved until after 2 hours into the jar test process. Arias and Summers (2014) explored how coagulation of DOM influences DBP formation and removal by adding chlorine at different locations. In this work, upon chlorination, halogenated organic matter (HOM) concentrations were measured prior to coagulation, during coagulation, after coagulation, and after filtration. As more DOM had been removed from solution, i.e., more treatment, the DBP yields were lower and lower. If the speed of the DOM-coagulant reaction is known, then an earlier time of chlorination may be applicable. Chlorinating earlier in a treatment plant would allow for drinking water utilities to meet the EPA mandated CT (concentration*time) disinfection criteria at lower chlorine doses by increasing contact times.

There are three other processes that may be affected by DOM coagulation kinetics; the use of powdered activated carbon (PAC), disinfection and DBP formation, and filtration. A common practice is to add PAC at the same time as coagulants to remove seasonal taste and odor (T&O) compounds 2-methylisoborneol (MIB) and geosmin. DOC competes with micropollutants (MPs) and T&O compounds for sites on PAC (Hepplewhite, et al., 2004) (Cho, 1996). Cho (1996) hypothesized that final DOC of a PAC treatment process is directly affected by the initial DOC and developed a model to predict DOC. While the bulk DOC competes with MPs, Ho and Newcombe (2005) state that the small size fraction (<300 Da) is the stronger competing size fraction. Coagulation can remove 50% or more of the DOM from some waters, so delaying PAC addition may be favored if enough of the strongly competing DOM size fraction has already been removed.

The EPA mandates the use of primary and secondary disinfectants to assure that minimal microbial activity is ingested upon water consumption. Some of the microbes which are found in drinking water can cause health effects and in extreme cases death. Primary disinfection is met by achieving the proper dose and contact time. Secondary disinfection is required to minimize regrowth within distribution systems and is generally mandated by distinct chlorine residual at the end of a distribution system. While disinfection is a vital process to maintain safe, clean water, there are negatives associated with the use of chlorine. One of the daily challenges for drinking water utilities is to meet regulatory constraints for DBPs. If there can be an enhancement of the chlorination process then utilities may save money, reducing customer costs.

The use of direct filtration for DOM removal may also be impacted by DOM coagulation kinetics. In direct filtration, coagulated water is applied directly to the filter. In some cases, it is first flocculated and in other, flocculation is bypassed.

5.1.2 Problem Statement

The kinetics of DOM removal during coagulation are not well understood. Point of PAC addition and primary disinfectant addition will likely be impacted by the organic matter (OM) state. If OM is in the dissolved state, i.e., DOM, then it may likely negatively impact these processes. If it is in the sorbed to or co-precipitated state associated with coagulant flocs, then the OM may be less of a problem. An understanding of the impact of influent water quality parameters and coagulation conditions on the kinetics is also important, as source water can exhibit seasonal variability in water quality and different mixing conditions and/or coagulant dose may be required to meet adequate DOM removal.

5.1.3 Research Objectives

The overall objective is to assess the kinetics of DOM coagulation and the specific objectives include examining the impact of influent water quality and operational parameters (coagulation conditions) on DOM removal kinetics and how PAC performance and DBP formation are impacted by DOM coagulation kinetics.

5.1.4 Approach

Bench-scale jar tests were used to address these objectives. DOM samples were taken at times representative of rapid mixing, flocculation and sedimentation. Eight waters with a range of water quality were evaluated. Four water quality parameters (pH, turbidity, temperature, and molecular size) and three operational parameters (mixing speed, coagulant type, and coagulant dose) were varied to assess their impact on DOM coagulation kinetics.

5.2 Methods

5.2.1 Organic Carbon

TOC and DOC concentrations were measured in accordance with Method 5310 C (Standard Methods, 1998). For DOC, samples were collected and immediately filtered through a 0.45 µm membrane filters (Pall Life Sciences). Filters were rinsed with at least 250 mL of reverse osmosis water to assure that no carbon leaching would take place. If the samples were not measured the same day as generation, then they were stored at 4°C. All TOC or DOC analysis was performed within three days of sample collection.

Analysis took place on a Sievers 5310 C Laboratory Total Organic Carbon Analyzer and the DataPro 5310 C soft was subsequently used to process the data. Samples were analyzed in groups of three or four with a blank in between to assure that operation was stable and there was no organic carbon carryover from previous samples. The instrument was calibrated in accordance with the Operations & Maintenance manual that accompanied the instrument upon installation. Quality assurance and quality control “test runs” were performed on a monthly basis to assure that drift over time was minimal.

5.2.2 UV$_{254nm}$ Absorbance

Ultra-violet absorbance at 254 nm (UVA$_{254}$) was measured using a DR/4000 Spectrophotometer produced by HACH. Samples were analyzed using a 1-cm quartz cell and absorbance values were reported with units of cm^{-1} as spectral absorbance coefficients. Samples were taken directly out of the same vials that were run on the Sievers TOC Analyzer. UV analysis was preformed within a week of sample collection. Samples were periodically tested at larger intervals to assure that the samples were stable and the UV reported is representative. If samples were not measured the same day as collection, then they were stored at 4°C.

5.2.3 Turbidity

Turbidity was measured in accordance with Method 2130 B (Standard Methods, 1998) using a 2100N Turbidimeter (HACH Company). Turbidity measurements are reported as nephlometric turbidity units (NTU) and were measured on whole, unfiltered water. Measurement vials were stored dry at room temperature and pre rinsed with de-ionized water and dried before use to assure no dilution of samples.

5.2.4 pH

pH was measured using a Denver Instruments, model 220 pH probe. The pH probe was calibrated weekly with pH values of 4, 7, and 10. This range of pH allows for the full range of values that are expected throughout the tests. Measurements were made by directly inserting the probe into each batch system immediately after sedimentation.

5.2.5 DBP Formation Tests and Analysis

THM and HAN concentrations were carried out in accordance with EPA Method 551.1 while for HAAs EPA Method 552.2 was used. 60 mL sample vials were rinsed with deionized water and muffled at 550 °C for 3 hours. Prior to sample collection, 6 mg of ammonium chloride was added to the vials to quench the formation of DBPs upon sample collection.

Samples were analyzed within one-week of collection on an Agilent 8890 series gas chromatograph (GC).

5.2.6 Batch Experiments (Jar Tests)

Batch experiments were performed using a jar test apparatus (Phipps & Bird) that allows for set mixing times at specific mixing speeds. Standard jar test experiments for coagulation involve adding coagulants at different concentrations in different jars and varying the mixing speed and time to simulate the rapid mix, flocculation and sedimentation processes. The jar tester apparatus used automatically changed mixing speeds and held constant speed for a set time. For all tests, the rapid mix regime was for one minute at 290 rotations per minute (rpm). The rapid mix was followed by two distinct flocculation stages both for ten minutes. The first mixing regime was set for 55 rpm while the second was set for 25 rpm. Following the dual flocculation stages there was a thirty-minute sedimentation period. This procedure will be referred to as the standard jar test protocol (SJTP), and the entire test lasts fifty-one minutes. Immediately after sedimentation, samples were collected using syringes and filtered through a 0.45 µm membrane filter (Pall Life Sciences). Rectangular containers (Phipps & Bird) with a capacity of 2 liters were used.

The alum used was hydrated aluminum sulfate ($Al_2(SO_4)_3$*$18H_2O$) from Fisher Scientific. The ferric used was hexahydrate ferric chloride ($FeCl_3$*$6H_2O$) also from by Fisher Scientific. The PAC type used was bituminous based WPH PAC.

In the coagulant alone and PAC alone experiments, the alum or PAC addition was at the beginning of the test. For the coagulation followed by PAC experiments, the jar tests were run under the conditions specified above with 2 liters of water and, after the sedimentation phase, water was decanted and dosed with PAC under the same mixing conditions. These tests were performed for an additional 51 minutes and subsequently sampled and filtered immediately after the second sedimentation period.

In the delayed chlorination experiments a slightly amended STJP was used. In these tests chlorine was added simultaneously with the alum and one minute after alum (immediately after the rapid mix). At this point the water is still moving close to the high rotational speed of rapid mix to provide good mixing for chlorine.

In experiments where temperature was varied and held constant during the jar test, temperature was monitored over the entire 51-minute jar test. In the low temperature case, water was stored in a freezer at 4 °C for 3 hours. The test jar was fitted with a thermometer. The test started with water at 9 °C and finished with water at 11 °C so an average of 10 °C was assumed. Similarly, at 30 °C a thermometer was used to monitor drift, starting at 31 °C and ending at 29 °C. In the high temperature case, a hot water bath was used to bring the water up roughly 10 °C.

5.2.7 Size Fractionation

The two size fractions investigated were isolated by a fractionation/concentration method where a recirculating tangential flow ultrafilter membrane with a molecular weight cutoff of 1,000 Daltons was utilized (Amicon regenerated cellulose 1 kDa cartridge). The molecular size stock of less than 1,000 Daltons was at a concentration of 21 mg-C/L and greater than 1,000 Daltons stock was at a concentration of 120 mg-C/L.

5.2.8 Error Analysis

The error associated with these experiments was calculated by performing about 20% of the jar tests in duplicate and sampling in duplicate for some of the sample points. The error used is the maximum operational plus analytical error observed across all jar tests. For DOC measurements, this is 6.5% (n=15), and for MIB measurements this is 5.8% (n=8).

5.3 Results & Discussion

5.3.1 Raw Water Quality

Table 5.1 presents the names, locations, and abbreviations of the waters and wastewater evaluated in this study. Influent water quality values are presented in Table 5.2. A wide range of influent water quality was targeted in this study. The DOC concentrations varied from 8.0 to 2.3 mg-C/L. Alkalinity values range from 17 to 128 mg-$CaCO_3$/L. Influent pH values range from 6.9 to 8.6 and SUVA values range from 1.6 to 3.1 L/mg-C/m.

Table 5.1: Abbreviations and locations for source water.

Name	Location	Abbreviation
Boulder Creek #1	Boulder Creek at Ebben G. Fine Park May ‘14	BC1
Denver Water #3	Ralston Reservoir April '14	DW3
Fort Collins Baseline	Cache la Poudre River April ‘14	FCB
Denver Water #2	Ralston Reservoir Dec '13	DW2
Greely-Loveland Reservoir	Greeley Reservoir Early-June '14	GLR
Boulder Creek #2	Boulder Creek at 28th St. Bridge June '14	BC2
Boulder Reservoir	Boulder Reservoir Mid-June '14	B.Res
Big Elks Meadow Large Size Fraction	Big Elks Meadow, Fractionated June '12	>1K BEM
Big Elks Meadow Small Size Fraction	Big Elks Meadow, Fractionated June '12	<1K BEM
Denver Water #4	Ralston Reservoir September '14	DW4
Boulder Wastewater	Boulder 75th St. Treatment Plant Late-Sept. '14	BWW
University of Colorado Pond	Holding pond on University of Colorado at Boulder main campus June '14	CUP

Table 5.2: Raw water quality for waters investigated in the kinetic section.

Raw Quality	DOC (mg-C/L)	UVA254 (cm^{-1})	SUVA (L/mg-C/m)	Turbidity (NTU)	Alkalinity (mg-$CaCO_3$/L)	pH
BC1	5.4	0.166	3.1	9.6	17	6.9
DW3	4.4	0.107	2.4	11.3	25	7.4
FCB	3.8	0.105	2.7	6.2	35	7.5
DW2	7.5	0.211	2.8	36.5	35	7.7
GLR	8.0	0.124	1.6	3.5	128	8.6
BC2	2.3	0.072	3.1	3.1	24	7.2
B.Res	4.7	0.088	1.9	2.8	114	8.5
>1K BEM	6.5	0.169	2.6	-	-	7.6
<1K BEM	6.5	0.116	1.8	-	-	7.5
DW4	4.0	0.109	2.8	5.5	30	7.3
BWW	6.8	-	-	-	-	8.1
CUP	3.2	0.097	3.0	15.6	30	7.3

5.3.2 Coagulation Dose Response Curves

Coagulation dose response curves for jar tests of four of the source waters are shown in Figure 5.1 expressed as DOC concentration and in Figure 5.2, expressed as normalized DOC concentration (DOC/DOC_0). For these four waters 45% TOC removal is required by the EPA (Table 2.1). Coagulation conditions for these waters were selected to yield 45 % TOC removal, and different doses are required to reach that removal. BC1, DW2, and DW4 can all reach the 45% removal at a dose of 40 mg/L, but DW3 required a higher dose. While both of the DW3 points at 40 mg/L are close together, there is some level of variability associated with replicating coagulation for on DOC removal. All of these waters yielded a plateau of removal in the dose range of 40 to 80 mg/L. Given this range, a dose of 40 mg/L appears to be more economical for drinking water utilities. While these waters show the same general behavior, other waters with a higher alkalinity and DOC, such as GLR, displayed different removal behavior and only 30%

removal is required. There is a difficulty to coagulate organics in high alkaline water as the pH remains high at given dose compared to a lower alkaline water. For the sake of consistency, a standard dose of 40 mg/L was used in all cases in the kinetic study. This allows for differences in removal based on influent character.

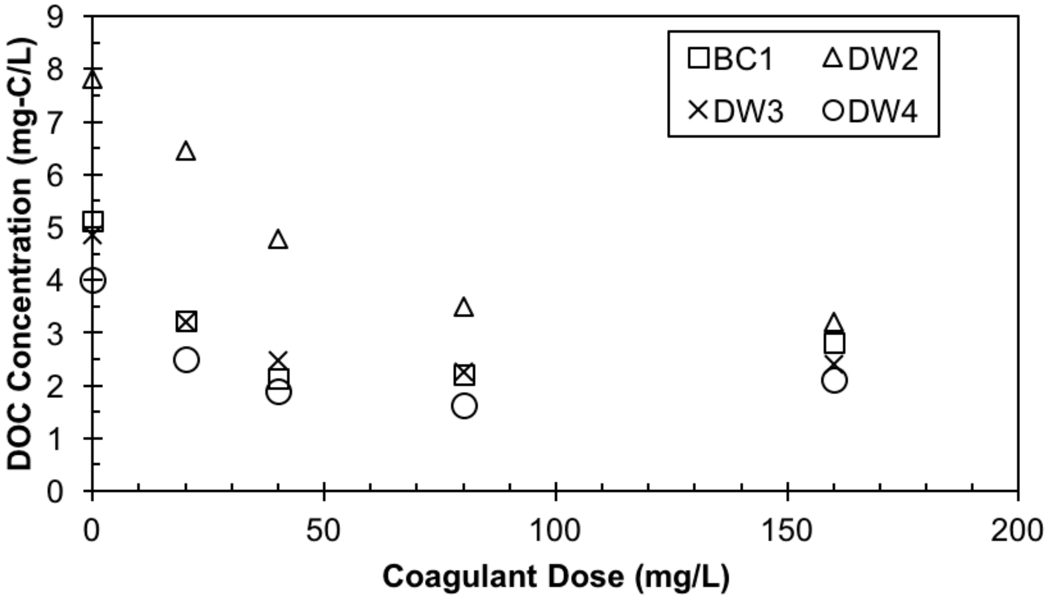

Figure 5.1: Coagulation response curves for four waters, DOC concentration response curve.

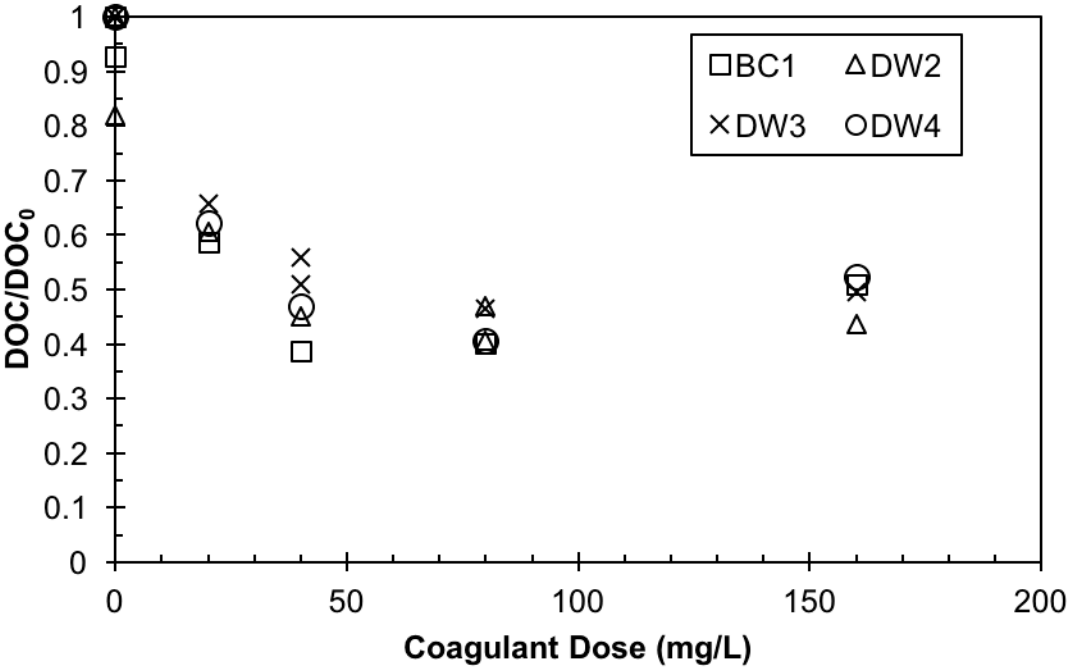

Figure 5.2: Coagulation response curves for four waters, normalized DOC concentration.

5.3.3 Raw Water Coagulation Kinetics

Eight surface waters and two different DOM size fractions (<1kDa, >1kDa) (Table 5.2) were investigated as part of the DOM coagulation kinetic study. In addition to these waters, influent and effluent of a wastewater treatment process were also examined.

The DOM coagulation kinetics of eight waters are presented in Figures 5.3a and 5.3b. The endpoint of DOM coagulation varied from 25% removal to 60% removal. The endpoint was impacted by the wide range of water qualities represented by these waters. However, little systematic change in the DOC removal occurred after one minute into the process (rapid mix). The results indicate that after the rapid mix stage of coagulation, DOC had reached equilibrium and no additional removal could be measured, even at the end of the sedimentation phase. These results are similar to those found by Arias and Summers (2003) for the one water that they studied. For all waters examined, sample times were chosen to correlate with mixing regimes changes and one sample point was selected in the middle of the first stage of flocculation. Figure 5.4 presents the time-scale for each of the mixing regimes within the testing protocol discussed in section 5.2.6. Each water had a different influent water quality and subsequently, at a dose of 40 mg-alum/L different endpoints of coagulation.

Along with DOC, the other water quality parameter that utilities monitor through flocculation is turbidity. Turbidity kinetics are difficult to measure within this time scale; particles continuing to coagulate and flocs continue to grow within the sample vial. Additionally, the objective of staged flocculation is to promote floc growth so that smaller particles can grow and settle out over time within the sedimentation process. Measuring turbidity during any stage of flocculation prior to sedimentation can provide insight to the size or abundance of flocs, but not the water’s equilibrium turbidity after sedimentation is complete.

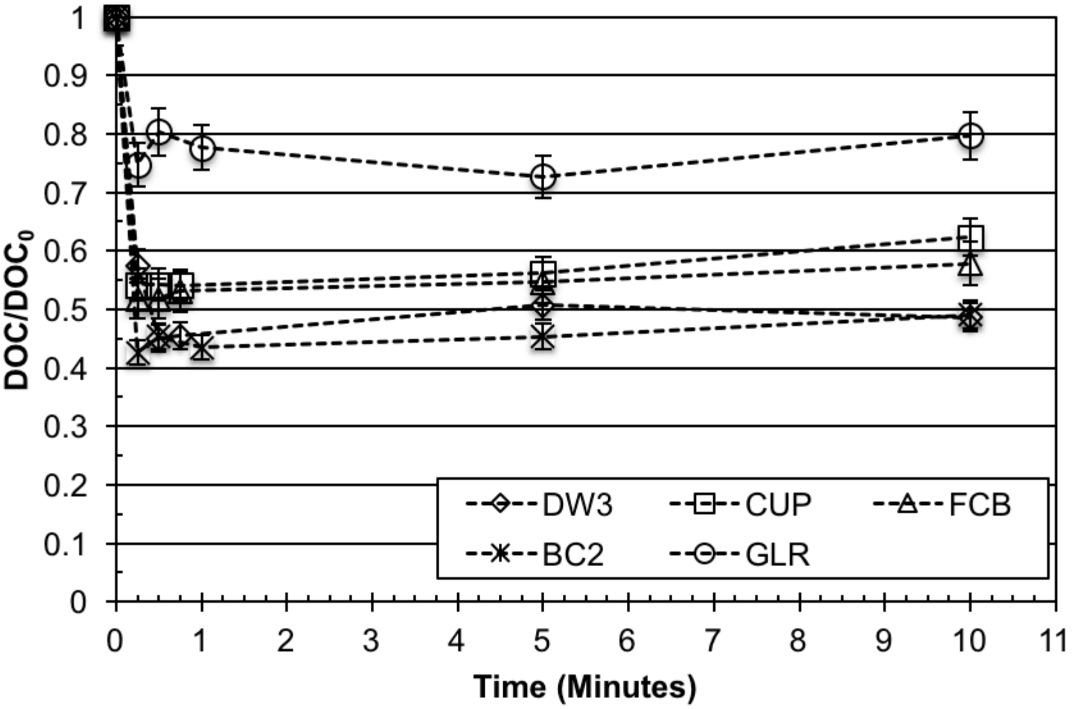

Figure 5.3a: Normalized DOM coagulation kinetics for five waters at an alum dose of 40 mg/L with three sample points taken below 1 min.

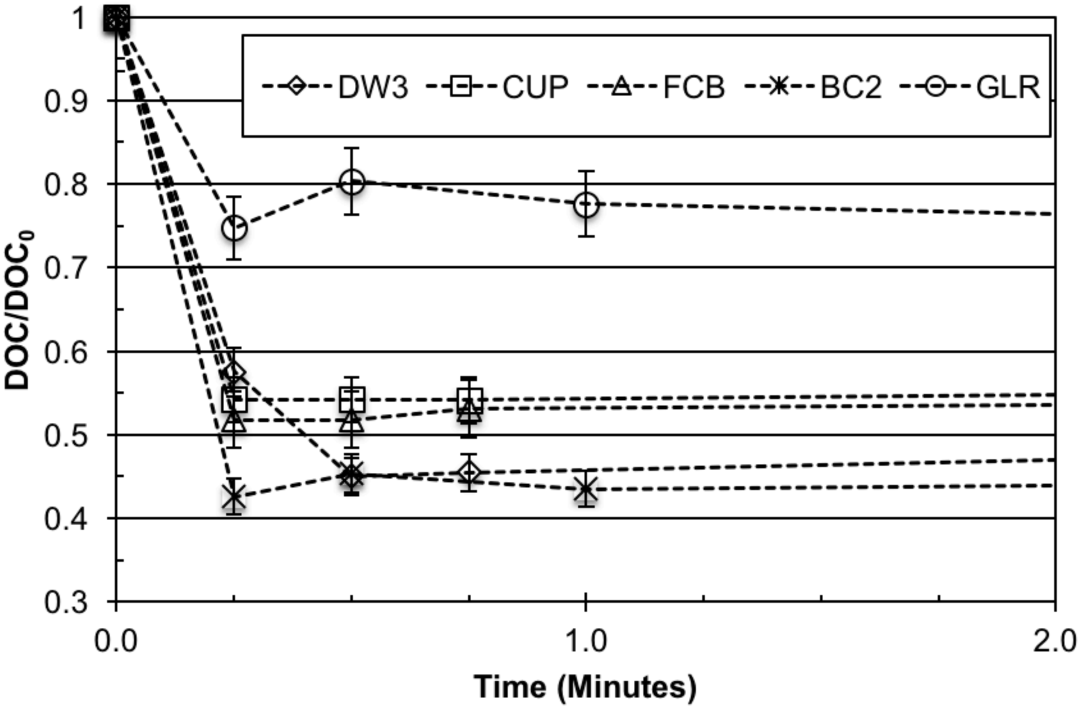

Figure 5.3b: Normalized DOM coagulation short-term kinetics for five waters at an alum dose of 40 mg/L with three sample points taken below 1 min.

The results in Figure 5.3b show that equilibrium DOC is reached within the first minute of rapid mix, but how quickly in that minute does equilibrium occur? Sampling points within the first minute of rapid mix, 15 seconds, 30 seconds, and 45 seconds, were measured, to further investigate the DOM coagulation kinetics. The short-term results, shown in Figure 5.3b, indicate that the DOC removal kinetics are complete in less than 1 minute. Sampling and measuring DOC this quickly is operationally difficult. Once a sample had been drawn from one of the batch systems (jars), it was immediately filtered through a 0.45-micron filter. However, in the sample syringe, the water continued to coagulate. To account for this, samples were removed from the jars 5-7 seconds before filtration i.e., 30-second sample point was syringed out of the batch system at 23-25 seconds and filtered by 30 seconds.

Figure 5.4 displays early time points of DOM coagulation kinetics using normalized DOC concentration. In addition, the DOC removals at 5 minutes and 10 minutes were also measured and compared to the “long” kinetic tests. In these tests, by 15 seconds, DOC reached equilibrium concentrations for the five waters studied.

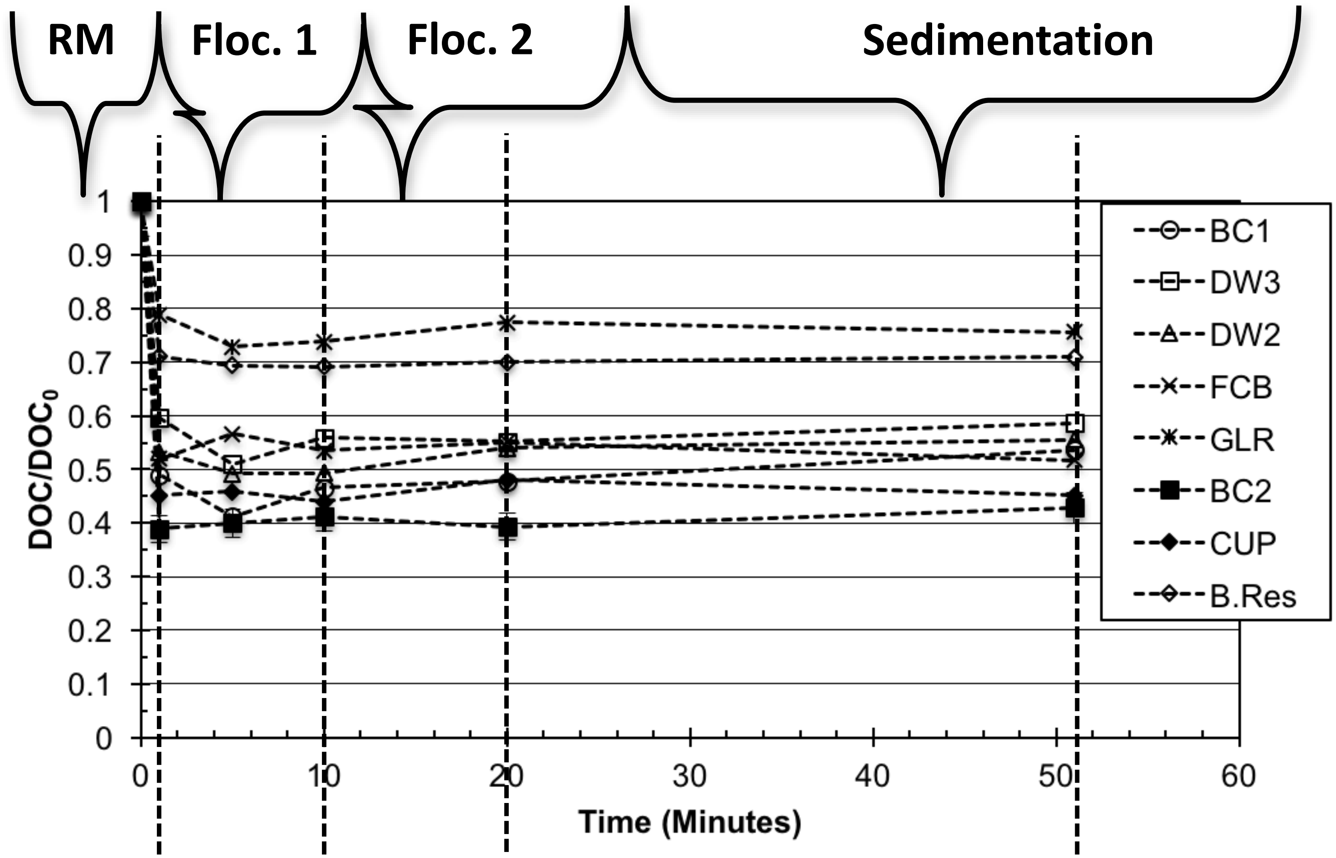

Figure 5.4: DOM coagulation kinetics at an alum dose of 40 mg/L. The labels at the top of the figure depict the different mixing regimes within the coagulation/flocculation/sedimentation process.

5.3.4 Impact of Water Quality and Operational Parameters

The results in Figure 5.4 indicate that source water type has no impact on the kinetics of DOM coagulation. However, a systematic variation on water quality and operational parameters could possibly show different results. Three operational and four water quality parameters were examined for their potential impact on DOM coagulation kinetics. The three operational parameters were rapid mixing speed, coagulant type (alum versus ferric) and coagulant dose, and the four water quality parameters investigated were temperature, turbidity, pH, and DOM molecular size.

Both the effect of mixing speed and temperature on DOC coagulation kinetics can be seen in Figure 5.5. Three mixing speeds of 55 rpm, 125 rpm, and baseline of 300 rpm were investigated. It was found that the different mixing speeds did not affect the kinetics nor the extent of DOM coagulation. After one minute, all of the DOC that was removed by the end of sedimentation was also completely tied up in the floc structure and filterable. Three temperatures examined were the baseline-room-temperature of 20 °C, and 10 °C and 30 °C. The results at the high temperature showed slightly less removal at all times compared to the other runs, but removal after 1 minute was not different than that at 51 minutes in any of the three runs.

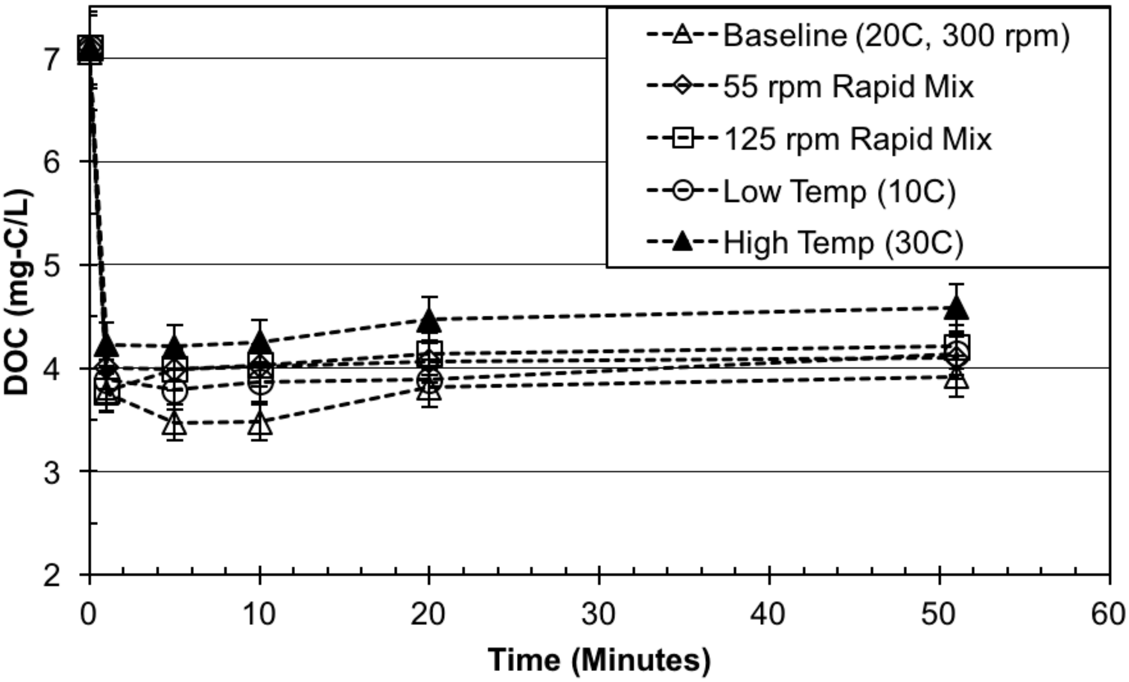

Figure 5.5: Effect of rapid mix speed and temperature on DOM coagulation kinetics for DW2.

Figure 5.6 displays the impact of turbidity on DOM coagulation kinetics. It was found that there was no impact of turbidity on kinetics of DOM coagulation. This is a significant finding; previous research and published literature has pointed to the formation of flocs around particles to be slower when turbidities are low and faster when they are high (Water Quality and Treatment: A Handbook of Community Water Supplies 1990). If sweep coagulation was primarily responsible for DOM removal, then there should be some delay or DOM equilibrium being reached in the low turbidity water. However, this was not the case, pointing to co-precipitation as being the dominant mechanism.

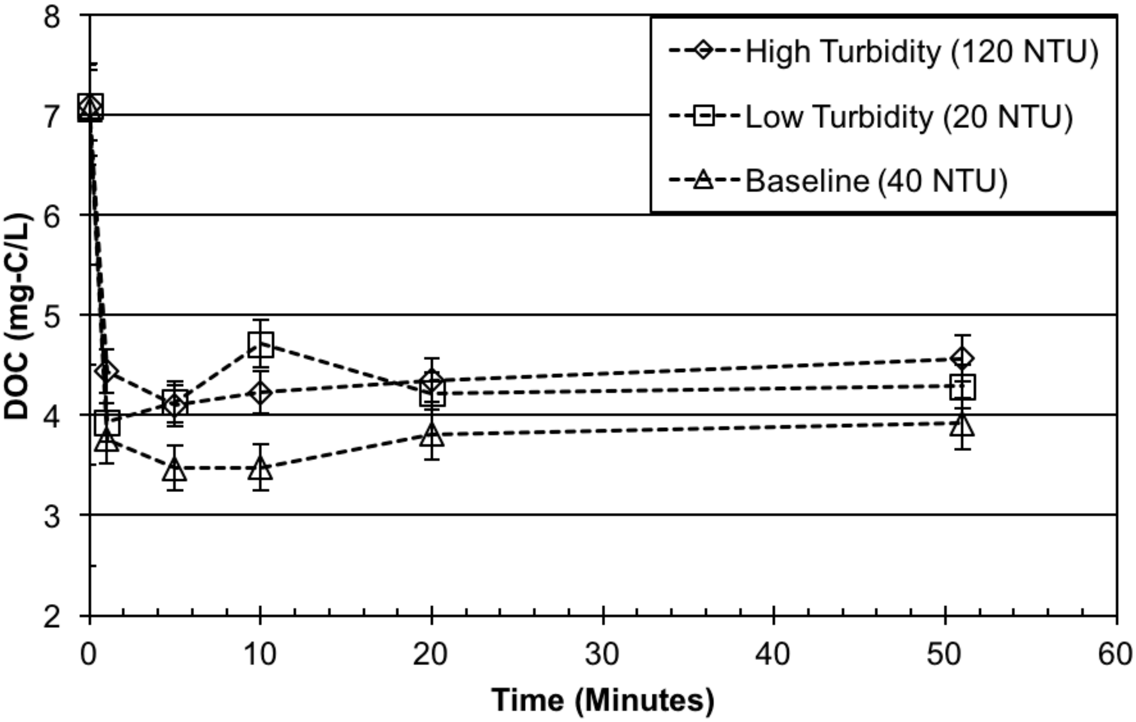

Figure 5.6: Effect of raw water turbidity on DOM coagulation kinetics for DW2.

Figure 5.7 shows the impact of coagulant type on DOM coagulation kinetics. After one minute of rapid mix for both ferric and alum coagulation, the same amount of DOC was removed or tied up in the floc structure as was removed by the end of sedimentation.

During the pH adjusted experiments, pH was monitored closely during the jar test. A surface water, B. Res., with a high initial pH and alkalinity was selected. pH was adjusted using hydrochloric acid at a stock concentration of 6 N. Acid was added one drop at a time until the desired pH values of 7.5 and 7.0 were reached. pH at the end of coagulation was measured to assure that the pH did not increase over the test and that typical pH reduction was seen. Typical pH reduction is around 1 pH unit at a dose of 40 mg/L alum. Figure 5.8 displays the effect pH has on DOM coagulation kinetics. As with the physical parameters examined, there was no effect of pH on DOM coagulation kinetics.

Figure 5.9 displays the dependence of DOM coagulation kinetics on coagulant dose. Four doses were chosen for this experiment; 10 mg/L, 20 mg/L, 30 mg/L and the baseline condition of 40 mg/L. Higher doses were not investigated because exploring higher doses is not economically sustainable from a utility standpoint. While coagulant dose has an impact on the equilibrium concentration of DOC, there was no impact on how quickly the DOC concentration reaches the equilibrium condition.

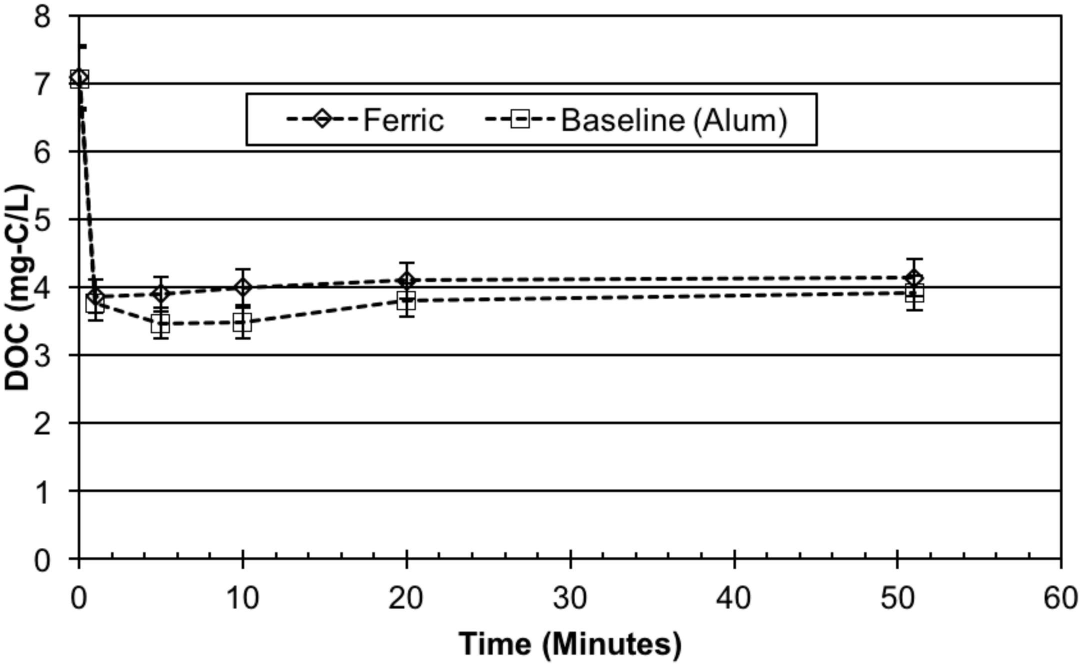

Figure 5.7: Influence of coagulant type on DOM coagulation kinetics for DW2.

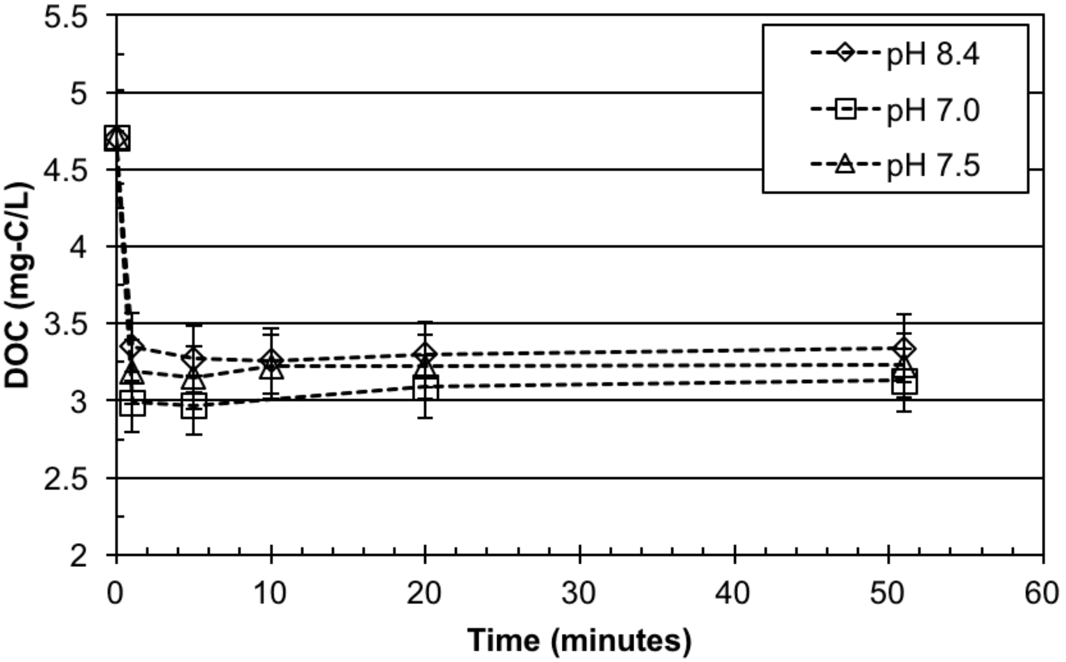

Figure 5.8: Influence of initial pH on DOM coagulation kinetics for B.Res water**.**

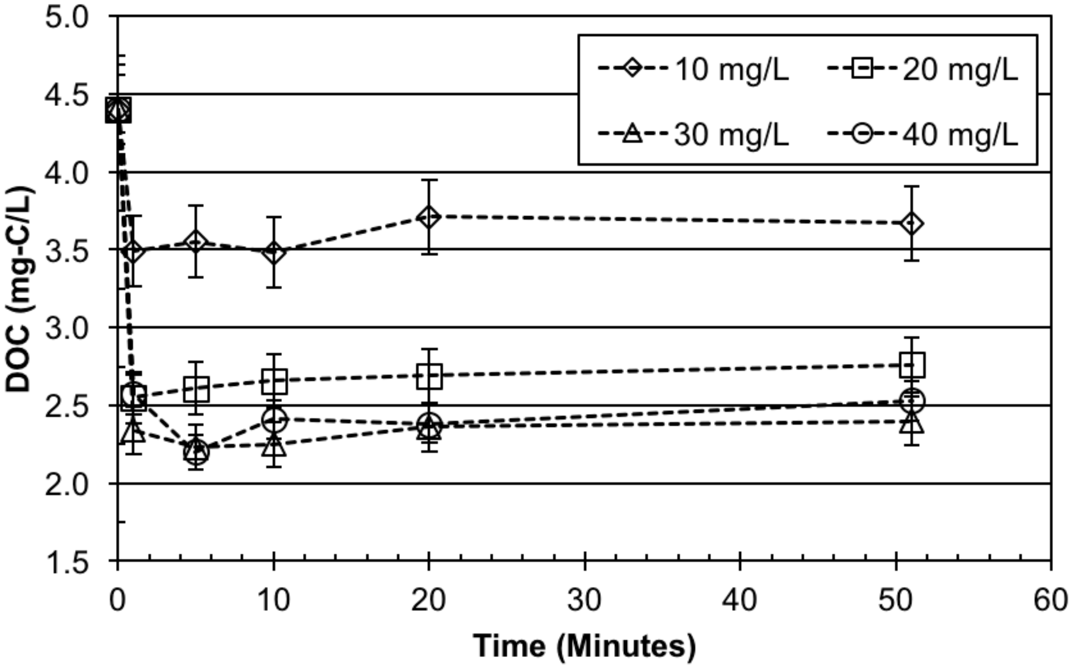

Figure 5.9: Coagulant dose impact on DOM coagulation kinetics for DW3.

The last parameter investigated was the influence of different DOM size fractions on DOM coagulation kinetics. Two size fractions were examined, less than and greater than 1000 Da (<1kDa, >1kDa). This molecular weight cutoff is consistent with work done by Shimabuku, et al. (2014).

Water was prepared from the stock concentrations to target the same DOC amount from both size fractions. Dechlorinated tap water was used as the background water matrix for the two size fractions. Results can be seen in Figure 5.10. While the smaller size fraction is more difficult to coagulate, at a dose of 40 mg/L there was only 20% reduction in DOC through the coagulation process, it did not take longer to reach equilibrium DOC concentration. Similarly, the large size fraction reached equilibrium of slightly more than 40% removal of DOC within the first minute. Coagulation of both fractions yielded higher DOC values after 20 minutes. No logical explanation for this behavior could be made.

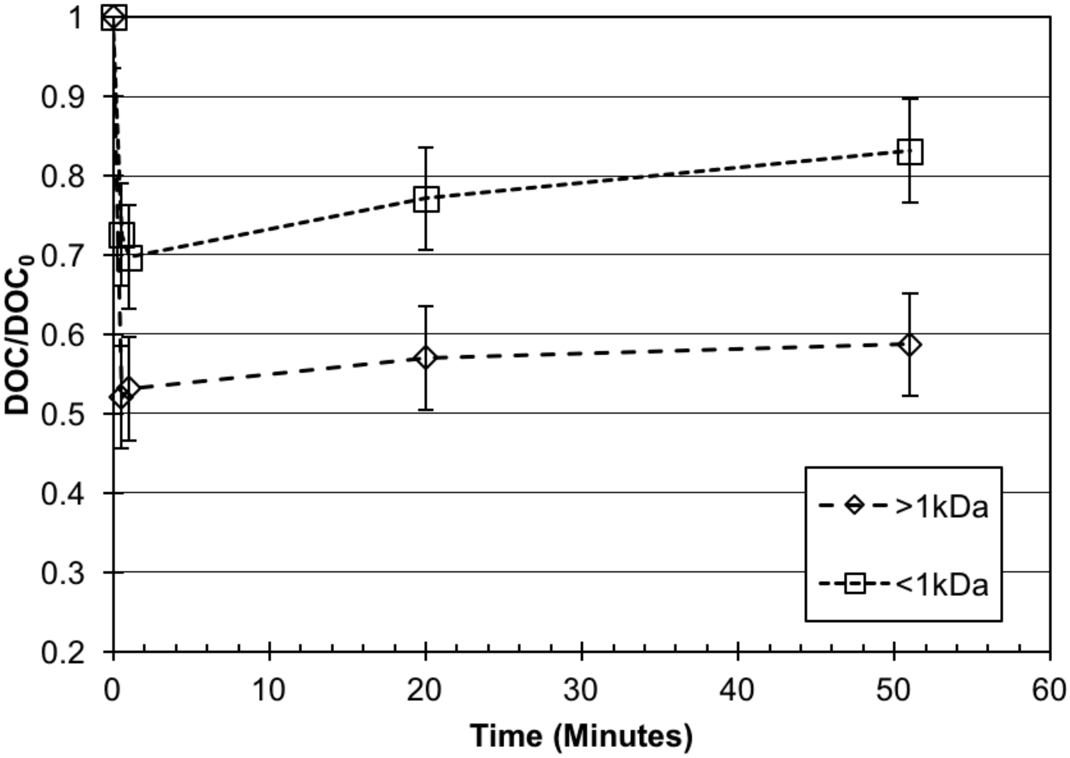

Figure 5.10: Normalized DOM coagulation kinetics for the two DOM size fractions studied.

In addition to the parameters evaluated in this section, the DOM coagulation kinetics of an influent and effluent of a wastewater treatment plant were examined. Jar tests were not conducted for coagulation dose response curves for the effluent; the influent did not show any removal of DOC even at a dose of 500 mg/L alum. The standard coagulant dose of 40 mg/L was applied to both influent and effluent wastewater. Figure 5.11 presents the kinetic data for DOC coagulation for both influent and effluent wastewater. Because the influent did not coagulate at all, there was no response. The wastewater effluent displayed the same behavior that the previous waters did, after 30 seconds of rapid mix, the DOC reached equilibrium concentration, or the same as after sedimentation.

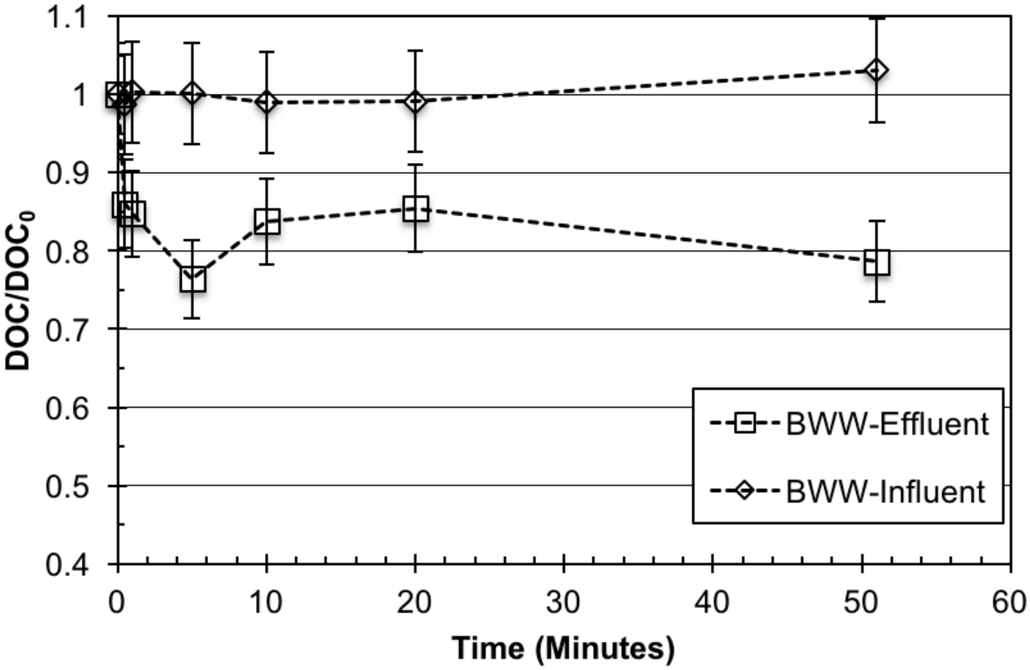

Figure 5.11: Normalized DOM coagulation kinetics for Boulder Wastewater effluent and influent.

5.3.5 Potential Implications on Other Treatment Processes

The rapid uptake of DOM during coagulation could have substantial implications on other drinking water treatment processes. There are three main processes that may be affected by these findings; a) PAC addition point, b) chlorine addition and the formation of DBPs and c) direct filtration.

The use of PAC is a typical control strategy for the removal of episodic organic contaminant problems, like the control of seasonal taste and odor (T&O) (Hepplewhite, et al., 2004). One common practice is to add PAC at the same point in a treatment plant as coagulants are added. If coagulation removes the DOC quickly, then PAC may potentially be applied after rapid mix to remove both DOC and T&O compounds, such as 2-methyliosborneol (MIB).

The results of delaying PAC addition by 5 minutes and by 51 minutes compared to adding PAC simultaneously with alum and coagulation alone are shown in Figure 5.12 for DOC removal. The alum dose was 40 mg/L and the PAC dose was 30 mg/L. In all cases the addition of PAC yielded about 10% more DOC removal compared to coagulation alone. However, there is no clear trend in the results to indicate where the optimal point of PAC addition is. Also, shown in Figure 5.12 is hierarchy of pH and SUVA values for these source waters. GLR has the highest pH and lowest SUVA value, which makes it difficult to coagulate. BC1 had the highest SUVA value and lowest initial pH and yielded the highest removal under these set dose conditions.

MIB removal results are shown in Figure 5.13. Coagulation alone did not remove MIB. With one exception, PAC without alum was found to yield best MIB removal performance. Literature states that influent DOC to a PAC adsorption process is important for determining the competitive effects of DOM and MIB (Cho 1996). When PAC addition was delayed 5 and 51 minutes, the influent DOC to the PAC adsorption process is the equilibrium DOC of the coagulation process, given the rapid DOC uptake. This indicates that coagulation does not remove the competing fraction of the DOM and leaves behind a size fraction that is strongly adsorbable. If coagulation removes 50% of DOC and none of it is competitive for adsorption sites on the PAC, then the DOC remaining is free to adsorb to the PAC without larger organics interfering.

These weak electrostatic forces holding DOM together may be overcome by the electrochemical pull of the aluminum hydroxide complexes (floc particles) to adsorb highly coagulable DOM, leaving behind smaller organic molecules that are free to compete with the MIB for adsorption sites. As a result, the addition of PAC in absence of coagulants is optimal for MIB removal followed by coagulation.

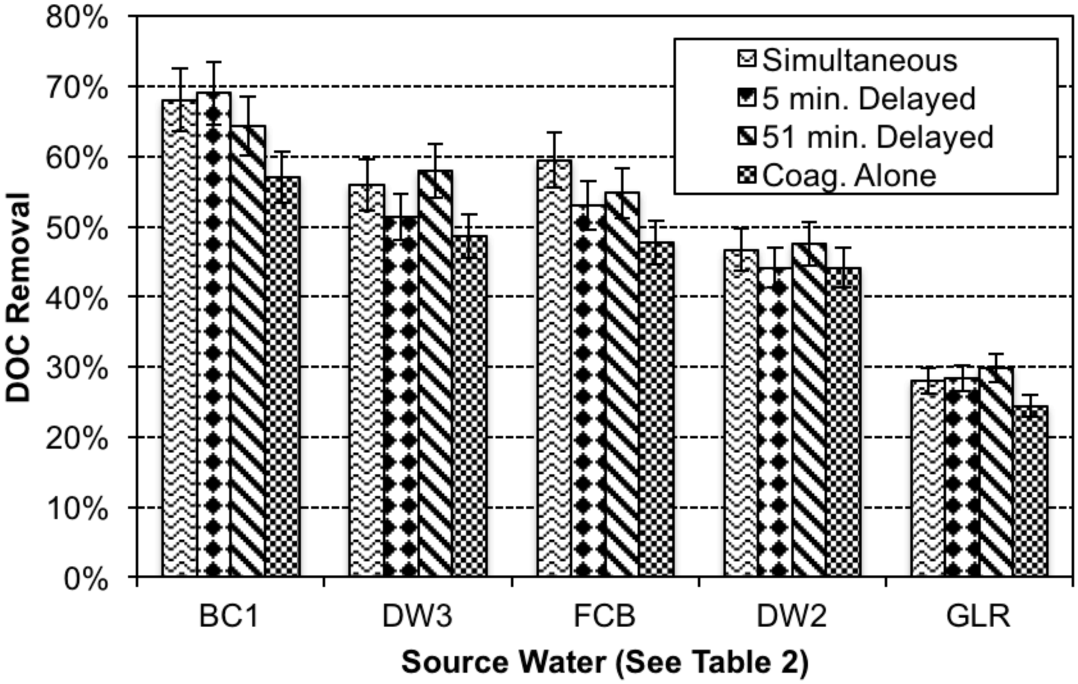

Figure 5.12: Impact of point of PAC (30 mg/L) addition on DOC removal compared to coagulation (40 mg/L) alone.

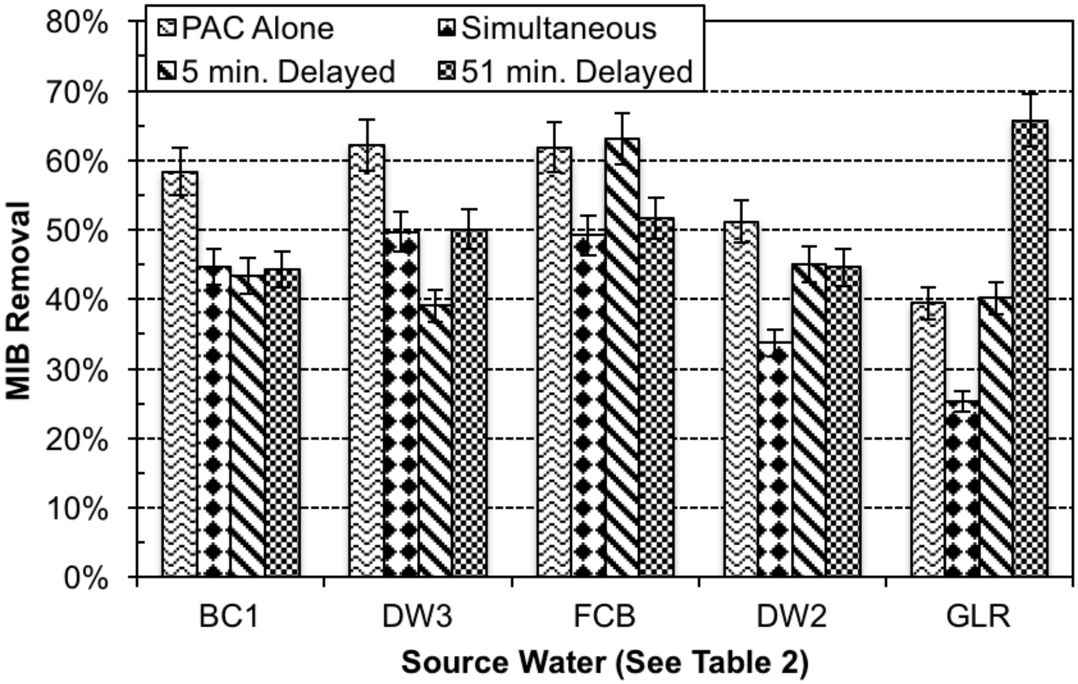

Figure 5.13: Impact of point of PAC (30 mg/L) addition on removal compared to coagulation (40 mg/L) alone.

All drinking water utilities treating surface waters must disinfect their water to meet mandated primary disinfection and maintain disinfectant levels within the distribution system. For many disinfectants, such as chlorine, DOM creates a significant demand and reacts with DOC to form DBPs, which are regulated on a mass concentration basis. If DOM is tied up in the floc structure then the potential for it to react with chlorine and form DBPs may be reduced and chlorine could be added earlier in a treatment process, allowing utilities to meet their mandated disinfection levels more easily with lower disinfectant doses

Adding chlorine simultaneous with alum in the rapid mix and after one minute of rapid mixing with alum was investigated on a proof of concept basis. DBP formation potential results can be seen in Table 5.3. Little difference was found in TTHM formation, but for HAA5 and HAN4, delayed chlorine addition yielded lower DBP formation. HAA5 formation is known to be more rapid than THM formation, which would explain the larger impact with the delayed chlorine addition.

Table 5.3: Disinfection by-product formation of combined chlorination/coagulation and delayed chlorination after coagulation of DOC.

DBP concentration (µg/L)	Combined Chlorine and Coagulant	Coagulant then Delayed Chlorine One Minute	Difference (%)
TTHM	115	110	4
HAA5	60	47	22
HAN4	2.3	1.9	17

These results agree with previous studies that examined chlorine applied to a system with flocs present. The DBP yields were lower than raw water yields (Arias and

Summers 2014). Their study, however, did not evaluate simultaneous addition of chlorine and alum. The concurrent addition of chlorine with alum is somewhat representative of raw water chlorination, with slightly less available DOC due to the quickness of reaching DOC equilibrium.

The final way in which these findings may have an impact on the drinking water community is the wider applicability of direct filtration. Direct filtration is a modification of conventional surface water treatment that removes the sedimentation process or, in contact filtration, removes both the flocculation and sedimentation processes (Water Treatment: Principles and Design 2012). If DOM is quickly retained in the floc, then substantial DOM removal could be achieved with direct filtration without the use of flocculation. Direct filtration is not practiced when source water turbidity is high, as high particle loading on filters can cause an increase in backwash frequency. However, in systems where turbidity is not of major concern, this research highlights the use of direct filtration to mitigate DOC levels and not require a large footprint for the plant, ultimately reducing capitol and operational costs.

5.4 Summary & Conclusion

In this study DOM coagulation kinetics were examined for eight surface waters, a wastewater influent and effluent, and two size fractions.

DOM coagulation kinetics showed the following:

- In eight surface waters equilibrium DOC concentrations were reached in one minute of rapid mix.
- Further investigation of five waters showed that equilibrium was reached within the first 30 seconds.
- Parameter investigation provides evidence that temperature, pH, rapid mix mixing speed, turbidity, coagulant type, and coagulant dose have no effect on the time-scale of coagulation in the range evaluated.

Applicability of coagulation kinetics demonstrated that:

- Although the organics are tied up in the floc structure very quickly, addition of PAC after organic equilibrium did not yield enhanced removal of organics or MIB.
- Adding chlorine after the organics had been tied up within the floc structure provided evidence that chlorine could be added during a flocculation process after rapid mix.
- Direct filtration may have a broader range of applicability if the main target for coagulation is dissolved organics.

Chapter 6
The Impact of the Point of PAC Addition on MIB Removal

6.1 Introduction

6.1.1 Background

Activated carbon (AC) has a high internal surface area, and as such can be effective for adsorbing hydrophobic organic compounds. It can remove specific organic compounds as well as a fraction of the overall dissolved organic matter (DOM), commonly measured by dissolved organic carbon (DOC). AC can aide in disinfection byproduct (DBP) control by removing organic precursor compounds that react with chlorine to form DBPs. In organic compound spill mitigation, compounds that have a high affinity to partition out of water, high partition coefficient, can be treated using AC. Powdered activated carbon (PAC) and granular activated carbon (GAC) are the two forms of AC used in water treatment (Summers, et al., 2010). PAC has a particle size below 0.01 mm, while GAC has a particle size of about 1 mm.

PAC is commonly used to mitigate taste and odor (T&O) causing compounds usually stemming from seasonal cyanobacteria blooms (Cook, et al., 2001), (Dixon, et al., 2011). Two main T&O compounds are 2-methylisoborneol (MIB) and geosmin. These compounds are not easily removed by coagulation, but readily adsorbed by PAC. Conventional practice is to add PAC during the rapid mix phase of a coagulation/flocculation/sedimentation process because there is already a process in place to mix the PAC into suspension and remove it during sedimentaton (Hepplewhite, et al., 2004). PAC is commonly added as either a dry powder or a water-slurry. PAC is not reactivated as it is difficult to separate from sludge that settles out in the sedimentation basin. Generally, PAC is not used on a continuous basis as it can be expensive and can contribute to membrane and filter clogging (Summers, et al., 2010).

Coagulation is historically used for particle and DOM removal, and has a high affinity for removing DOM from surface waters. Compared to PAC, coagulation is a more economic approach for DOM control. However, only a fraction of DOM is amenable to be removed by coagulation. PAC has the potential to yield additional DOM removal, beyond that achieved by coagulation. The U.S. EPA requires that surface water treatment plants, with TOC levels above 2 mg/L, remove TOC to reduce the formation of DBPs (Table 2.1). One of the best available technologies (BAT) per the EPA, for DOC removal, is coagulation. GAC filter-adsorbers are also recommended as a BAT for DOC removal. PAC and GAC have similar mechanisms for removal, but differ in the way in which they are used in a treatment plant.

While it is operationally easy to add PAC during a rapid mix stage in a coagulation process, little research has been published exploring the optimal PAC addition point in a treatment process. There have been a number of studies evaluating the use of PAC and potential limitations and interferences caused by DOM adsorption (Hepplewhite, et al., 2004), (Shimabuku, et al., 2014), (Cook, et al., 2001) (Volk, et al., 2000).

The main focus of this research is to evaluate the impact DOM of on MIB removal by PAC. DOM has a negative influence of MIB adsorption (Hepplewhite, et al., 2004). There are two distinct molecular size fractions of DOM, which may influence MIB adsorption. DOM with a molecular weight less than 300 Daltons are regarded as the competing molecular size (MS) fraction of organic matter and directly compete for adsorption sites on the PAC (Hepplewhite, et al., 2004). The larger than 300 Dalton DOM will negatively impact MIB removal, but by a different mechanism. Larger DOM block tortuous channels that lead to the large pore structure within PAC. When channels are blocked, smaller organics and target compounds, like MIB, cannot penetrate deep into the pore structure and removal efficiency is decreased (Shimabuku, et al., 2014).

A model has been developed, predicting DOC and MIB concentrations from a PAC adsorption process (Cho, 1996). This model is discussed in Chapter 2 and relates MIB and DOC removal to the influent DOC concentration. This research postulated that as influent DOC concentrations increase, removal efficiencies for DOC and MIB decrease. The bulk DOC has a highly competitive nature, but, as other research has shown, the two MS fractions compete differently (Shimabuku, et al., 2014).

Shimabuku, et al. (2014) evaluated the effect of two MS fractions, with a molecular weight cutoff of 1,000 Daltons (1 kDa). A large (>1 kDa) and small (<1 kDa) size fraction were evaluated for their effect on MIB adsorption. It was found that the fluorescence index (FI) can be used to determine the competitive nature of the bulk organic matter. Generally, lower FI values cause less interference and higher FI values result in more interference. FI is a good indicator of organic matter source (McKnight, et al., 2001) with higher FI values (1.9) corresponding to aquatic or microbial sourced organic matter and lower FI values (1.4) corresponding to terrestrial derived organic matter. However, because FI was found to have this relationship with MIB adsorption and to what level the organic matter competes, an argument can be made that molecular size may be a better interpretation of FI, with lower FI values meaning larger molecules and higher FI values meaning smaller molecular weight in drinking water applications (Korak, et al., 2015). Therefore, FI can be used as a predictor for the efficiency of MIB removal when PAC is used.

Water re-use is gaining momentum in the drinking water community in locations where water resources are scarce. There are many types of water reuse, but two main types of approaches for drinking water applications are indirect potable reuse and direct potable reuse (DPR). DPR involves taking primary wastewater and treating it to drinking water standards. Indirect potable reuse involves a natural buffer or barrier, such as river bank filtration or deep well injection. In order to generate public acceptance of DPR, it is important to implement redundant processes to provide multiple barriers for drinking water. When treating primary wastewater to a drinking water standard, multiple barriers are vital not only for public health, but for public perception.

Based on the results in Chapter 5, coagulation of DOM reaches equilibrium within the first 20 seconds of rapid mix. If DOM is removed by coagulation in 20 seconds, and is a main constituent in the water that hinders MIB adsorption, then delaying the addition of PAC to remove MIB should provide better removal. However, as shown in Figure 5.13, this is not the case. These results indicate that PAC performs best for MIB removal in absence of coagulants, or, prior to coagulants. While pre-treatment with PAC is the best option to remove peak MIB concentrations it is not clear how long prior to coagulation it should be added. Longer contact times yield more removal of DOC (Cho, 1996) but also require a larger footprint and higher costs.

6.1.2 Problem Statement

PAC has been widely applied to surface water to remove seasonal T&O compounds, such as MIB. Little research has been published to evaluate the optimal point of PAC addition in a water treatment process to remove organic contaminants

6.1.3 Research Objectives

- Evaluate surface waters spiked with MIB to determine the optimal point for PAC addition in and around the coagulation process.
- Examine the use of the fluorescence and the FI as an indicator of MIB removal through the process.

6.1.4 Approach

This research was conducted using a jar testing procedure described in Chapter 5.

6.2 Methods

6.2.1 Organic Carbon

TOC and DOC concentrations were measured in accordance with Method 5310 C (Standard Methods, 1998). For DOC, samples were collected and immediately filtered through a 0.45 µm membrane filters (Pall Life Sciences). Filters were rinsed with at least 250 mL of reverse osmosis water to assure that no carbon leaching would take place. If the samples were not measured the same day as generation, then they were stored at 4°C. All TOC or DOC analysis was performed within three days of sample collection.

Analysis took place on a Sievers 5310 C Laboratory Total Organic Carbon Analyzer and the DataPro 5310 C soft was subsequently used to process the data. Samples were analyzed in groups of three or four with a blank in between to assure that operation was stable and there was no organic carbon carryover from previous samples. The instrument was calibrated in accordance with the Operations & Maintenance manual that accompanied the instrument upon installation. Quality assurance and quality control “test runs” were performed on a monthly basis to assure that drift over time was minimal.

6.2.2 UV_{254nm} Absorbance

Ultra-violet absorbance at 254 nm (UVA_{254}) was measured using a DR/4000 Spectrophotometer produced by HACH. Samples were analyzed using a 1-cm quartz cell and absorbance values were reported with units of cm^{-1} as spectral absorbance coefficients. Samples were taken directly out of the same vials that were run on the Sievers TOC Analyzer. UV analysis was preformed within a week of sample collection. Samples were periodically tested at larger intervals to assure that the samples were stable and the UV reported is representative. If samples were not measured the same day as collection, then they were stored at 4°C.

6.2.3 Turbidity

Turbidity was measured in accordance with Method 2130 B (Standard Methods, 1998) using a 2100N Turbidimeter (HACH Company). Turbidity measurements are reported as nephlometric turbidity units (NTU) and were measured on whole, unfiltered water. Measurement vials were stored dry at room temperature and pre rinsed with de-ionized water and dried before use to assure no dilution of samples.

6.2.4 pH

pH was measured using a Denver Instruments, model 220 pH probe. The pH probe was calibrated weekly with pH values of 4, 7, and 10. This range of pH allows for the full range of values that are expected throughout the tests. Measurements were made by directly inserting the probe into each batch system immediately after sedimentation.

6.2.5 Fluorescence Measurements

A Hobriba FluoroMax-4 (Irvine, CA) fluorometer was run in S/R (signal/reference) mode using excitation and emission bandwidths of 5 nm and integration times of 0.25 s to collect fluorescence excitation and emission matrixes (EEMs). Lamp, Raman, and cuvette checks were completed at the start of each day to ensure reliable performance. Excitations went from 240 to 450 nm at 10 nm increments and emissions went from 300 to 600 nm using 2 nm increments. EEMs were corrected by blank subtraction, Raman normalization, instrument specific corrections, and inner filter corrections using UV spectra gathered with a Cary 100 Bio UV-vis spectrophotometer (Palo Alto, CA). The fluorescence index (FI), which is the ratio of emission intensities at 520 nm and 470 nm with an excitation of 370 nm (Korak, et al., 2015).

6.2.6 2-methylisoborneol

MIB is a nonionic compound. Log K_{ow} is 3.31 for MIB and it has a MW of 168 g/mol. ^{14}C MIB was obtained from American Radiolabeled Chemicals, Inc. (St. Louis, MO) and diluted with the respective cold compound (Sigmga Alrich, (St. Louis, MO)) to yield specific activities of 55 mCi/mmol. MIB activity was detected using liquid scintillation counting and had detection limits near 10 ng/L with a confidence level of 95% (Shimabuku, et al., 2014).

6.2.7 Size Fractionation

The two size fractions investigated were isolated by a fractionation/concentration method where a recirculating tangential flow ultrafilter membrane with a molecular weight cutoff of 1,000 Daltons was utilized (Amicon regenerated cellulose 1 kDa cartridge). The molecular size stock of less than 1,000 Daltons was at a concentration of 21 mg-C/L and greater than 1,000 Daltons stock was at a concentration of 120 mg-C/L (Shimabuku, et al., 2014).

6.2.8 Batch Experiments (Jar Tests)

Batch experiments were performed using a jar test apparatus (Phipps & Bird) that allows for set mixing times at specific mixing speeds. Standard jar test experiments for coagulation involve adding coagulants at different concentrations in different jars and varying the mixing speed and time to simulate the rapid mix, flocculation and sedimentation processes. The jar tester apparatus used automatically changed mixing speeds and held constant speed for a set time. For all tests, the rapid mix regime was for one minute at 290 rotations per minute (rpm). The rapid mix was followed by two distinct flocculation stages both for ten minutes. The first mixing regime was set for 55 rpm while the second was set for 25 rpm. Following the dual flocculation stages there was a thirty-minute sedimentation period. This procedure will be referred to as the standard jar test protocol (SJTP), and the entire test lasts fifty-one minutes. Immediately after sedimentation, samples were collected using syringes and filtered through a 0.45 µm membrane filter (Pall Life Sciences). Rectangular containers (Phipps & Bird) with a capacity of 2 liters were used.

The alum used was hydrated aluminum sulfate ($Al_2(SO_4)_3*18H_2O$) produced Fisher Scientific. The PAC type used was bituminous based WPH PAC (Calgon Carbon).

In the coagulant alone and PAC alone experiments, the alum or PAC addition was at the beginning of the test. For the coagulation followed by PAC experiments, the jar tests were run under the conditions specified above with 2 liters of water and, after the sedimentation phase, water was decanted and dosed with PAC under the same mixing conditions. These tests were performed for an additional 51 minutes and subsequently sampled and filtered immediately after the second sedimentation period.

In the experiments where PAC was applied prior to coagulation, jars were mixed at a constant paddle speed (55 rpm) for the allocated contact time. Then, the standard jar test procedure for rapid mix, flocculation, and sedimentation was applied.

6.2.9 Error Analysis

The error associated with these experiments was calculated by performing about one-fifth of the jar test in duplicate and by sampling in duplicate for some of the sample points. The error used is the maximum operational plus analytical error seen across all jar tests. For DOC measurements, this is 6.5% (n=15) and for MIB measurements this is 5.8% (n=8).

6.3 Results & Discussion

6.3.1. Raw Water Quality

Sources waters, described in Table 5.1, with a range of influent water quality parameters were targeted in this study. Table 6.1 presents the raw water quality parameters of the surface waters examined in this study. DOC concentrations varied from 2.3 to 8.0 mg-C/L. Alkalinity values ranged from 17 to 128 mg/L as $CaCO_3$. Influent pH values ranged from 6.9 to 8.6, SUVA values ranged from 1.6 to 3.1 L/mg-C/m, and FI values ranged from 1.40 to 1.88.

Table 6.1: Water quality parameters for the waters examined in this study.

Raw Quality	DOC (mg-C/L)	UVA254 (cm^{-1})	SUVA (L/mg-C/m)	Turbidity (NTU)	Alkalinity (mg-$CaCO_3$/L)	pH	FI
BC1	5.4	0.166	3.1	9.6	17	6.9	1.40
DW3	4.4	0.107	2.4	11.3	25	7.4	1.44
FCB	3.8	0.105	2.7	6.2	35	7.5	1.43
DW2	7.5	0.211	2.8	36.5	35	7.7	-
GLR	8.0	0.124	1.6	3.5	128	8.6	1.52
BC2	2.3	0.072	3.1	3.1	24	7.2	1.42
B.Res	4.7	0.088	1.9	2.8	114	8.5	-
>1K BEM	7.5	0.169	2.6	-	-	7.6	1.41
<1K BEM	5.7	0.116	1.8	-	-	7.5	1.59
BWW	6.8	-	-	-	-	8.1	1.88
CUP	3.2	0.097	3.0	15.6	30	7.3	1.44

6.3.2. Uptake Kinetics

In Chapter 5, it was demonstrated that delaying PAC addition by 5 and 51 minutes into a coagulation process did not yield higher removals of DOC or MIB. Previous research indicates that, if PAC is added after DOM coagulation, there would be less organic fouling of PAC sorption sites and subsequently higher MIB removals (Hepplewhite, et al., 2004), (Cook, et al., 2001). However, the results presented in Chapter 5 did not demonstrate that higher removal of MIB was achieved during simultaneous addition of PAC and coagulants. As shown in Figure 5.13, PAC had the highest efficiency for MIB removal in absence of coagulants. There are two possible explanations for this phenomenon.

One explanation is that the incorporation of PAC into the floc particle hinders bulk dispersion and reduces the ability of MIB to reach the PAC particle surface. This explanation is difficult to prove and research in the PAC field has yielded conflicting evidence for the effect of PAC incorporation into floc particles. One study evaluated trichloroethane (TCE) uptake by PAC in the presence of flocs (Graham, 1997), and demonstrated that PAC can be incorporated into floc particles without reducing the capacity of PAC to adsorb TCE.

Another explanation of this phenomenon is related to the mechanism of DOM coagulation by metal salts. Coagulants are acidic, reducing treated water pH and SUVA. SUVA is correlated with aromaticity of DOM and in turn the reactivity (Weishaar, et al., 2003). Aromatic compounds are believed to be more reactive than aliphatic compounds (Weishaar, et al., 2003). While there has been research demonstrating that SUVA can be used as an indicator for the degree of DOM coagulation, little is known about SUVA providing any indication of PAC adsorption capacity for DOM. Also, because SUVA is correlated with aromaticity, it is also correlated with molecular size (Weishaar, et al., 2003). Larger molecules traditionally have more aromatic moieties, so higher SUVA values mean larger organics. If the SUVA is reduced through a coagulation process, meaning the lower molecular weight, less reactive compounds remain in solution after coagulation, then the molecules remaining after coagulation could be the more strongly competing MS fraction.

The DOC removal kinetics, at a PAC dose of 30 mg/L and without a coagulant, for five waters, is shown in Figure 6.1. These results agree with previous studies; longer PAC contact times result in higher DOM removal (Cho, 1996). If longer contact times are preferred for PAC treatment and delaying PAC addition does not provide higher removal of DOM or MIB (see Figure 5.12 and Figure 5.13), then pre-treatment with PAC needs to be evaluated. This kinetic data may explain why, for some waters, simultaneous addition of PAC with coagulants performed better or the same for DOC removal (see Figure 5.12). As shown in Figure 5.3a and Figure 5.3b, after 20 seconds of rapid mix, the DOM has been tied up in the floc structure. PAC removal of DOM substantially increases from one minute to five minutes. This means that the DOM has not had enough time to be removed by PAC when the coagulable DOM fraction is tied up in the floc structure. This is due to different mechanisms of DOM removal by coagulation and PAC adsorption. Adsorption requires internal mass transfer into the pore structure of the PAC. Coagulation is a surface reaction involving co-precipitation and/or adsorption onto aluminum hydroxide flocs.

Figure 6.2 presents MIB removal by PAC alone at one minute and at fifty-one minutes of contact time for the five waters used in this study. In all waters examined, longer contact times of PAC with MIB provide significant enhanced removal (Cho, 1996). Cho’s model also has time as one of the independent variables affecting both DOC and MIB removal performance.

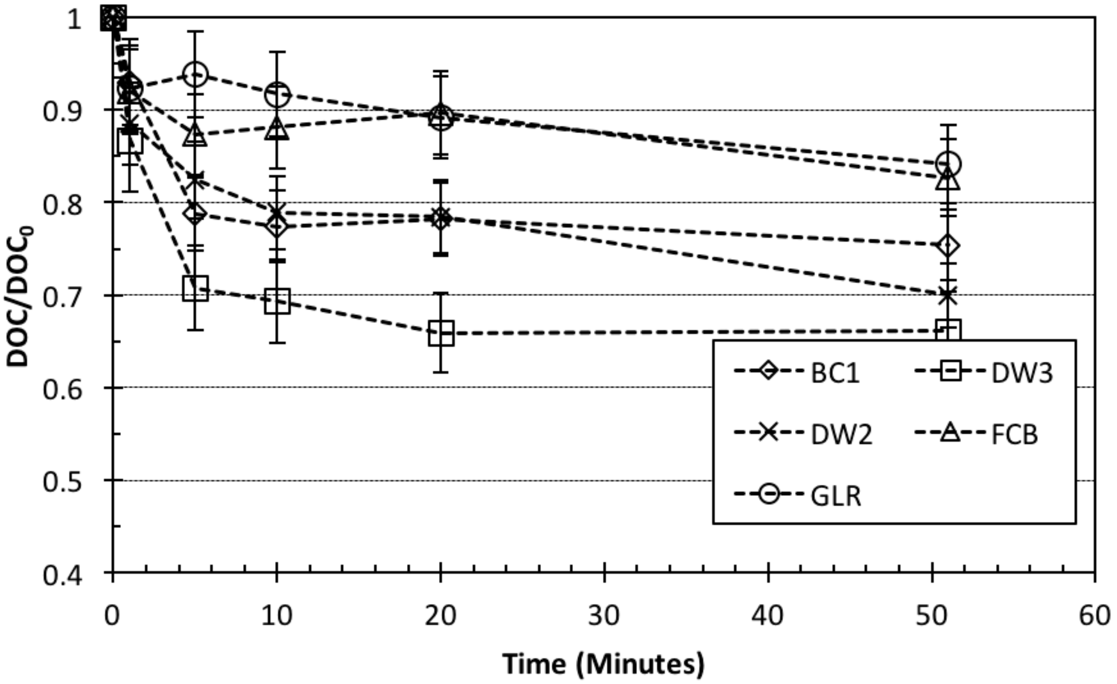

Figure 6.1: DOC removal kinetics at a PAC dose of 30 mg/L with no alum.

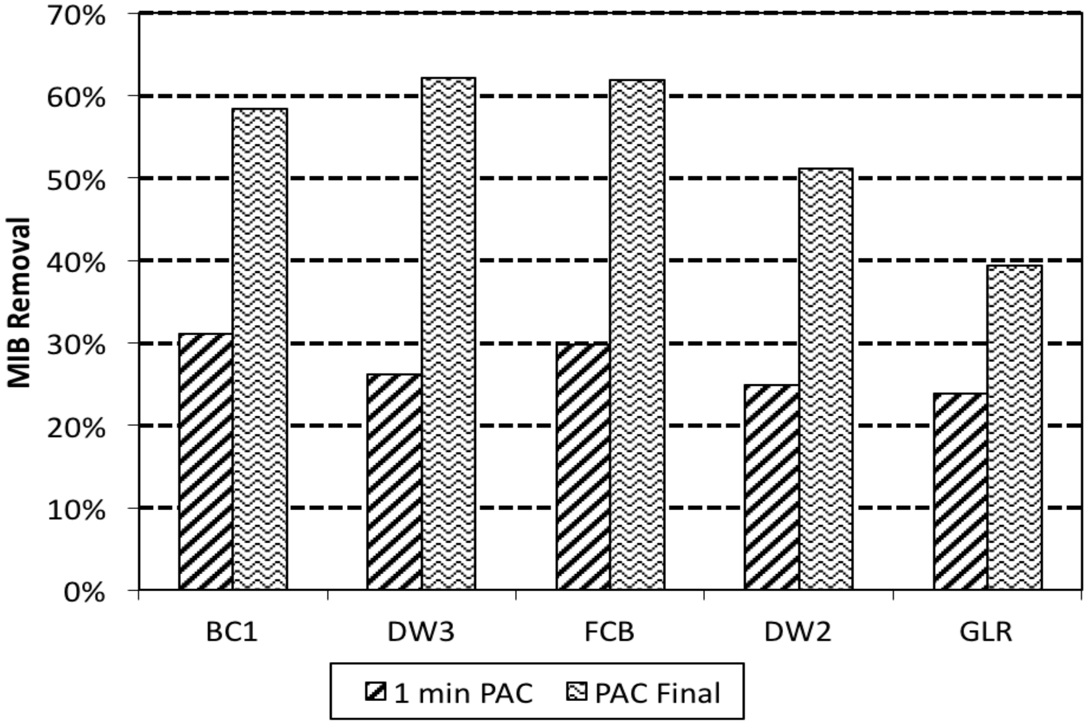

Figure 6.2: MIB removal at two contact times, 1 minute and 51 minutes, at a PAC dose of 30 mg/L with no alum.

6.3.3. PAC Addition Points

Based on the results in Chapter 5, delayed addition of PAC does not result in higher removal of either DOC or MIB. For MIB removal, PAC preformed the best in absence of coagulants, thus addition of PAC before coagulation needs to be examined. Figure 6.3 through Figure 6.5 present MIB and DOC removal for seven different PAC addition points: four PAC addition times before coagulation, one simultaneous (combined) addition, and two delayed addition times (5 minutes and 51 minutes) at a coagulation dose of 40 mg/L. In every case, earlier addition times of PAC provided additional MIB removal. This is may be attributed to the kinetics of MIB removal by PAC; longer contact times provide more MIB removal. Coagulation is not effective at removing MIB due to its aliphatic structure (Weishaar, et al., 2003). MIB volatilized in the control (no PAC) as indicated by around 25% removal of MIB over the 51-minute jar test procedure.

The differences in the observed removal of DOC can be attributed to differences in the raw water quality of these three waters. At a coagulant dose of 40 mg/L, DOM was not removed to the same extent in GLR as in other waters examined. GLR has the lowest raw water SUVA and the highest raw water pH and alkalinity. Waters with low SUVA, as well as waters with high pH and alkalinity, are hard to coagulate due to the mechanisms of DOM coagulation, co-precipitation and adsorption. FCB and BC2 both have moderate SUVA values (> 2.5 L/mg-C/m) and low alkalinities (< 60 mg/L as $CaCO_3$). FCB has a lower pH and a higher alkalinity than BC2. FCB presented less normalized removal of DOM during coagulation than BC2. Based on the results shown in Figure 6.3 through Figure 6.5, the optimal PAC addition time for MIB removal is between the 10 to 20 minutes prior to coagulation. However, because longer contact times require larger treatment systems and a larger capital investment, the 10-minute addition time is proposed as a more feasible point of PAC addition for MIB removal. The best removal of MIB, observed in all cases, is with PAC added one hour prior to coagulation. In this case, PAC has had enough time to remove MIB to a greater extent. Delayed addition is not optimal because coagulation removes a MS fraction of the DOM that does not strongly compete with MIB for sites on PAC, leaving behind the strongly adsorbing, small DOM molecules.

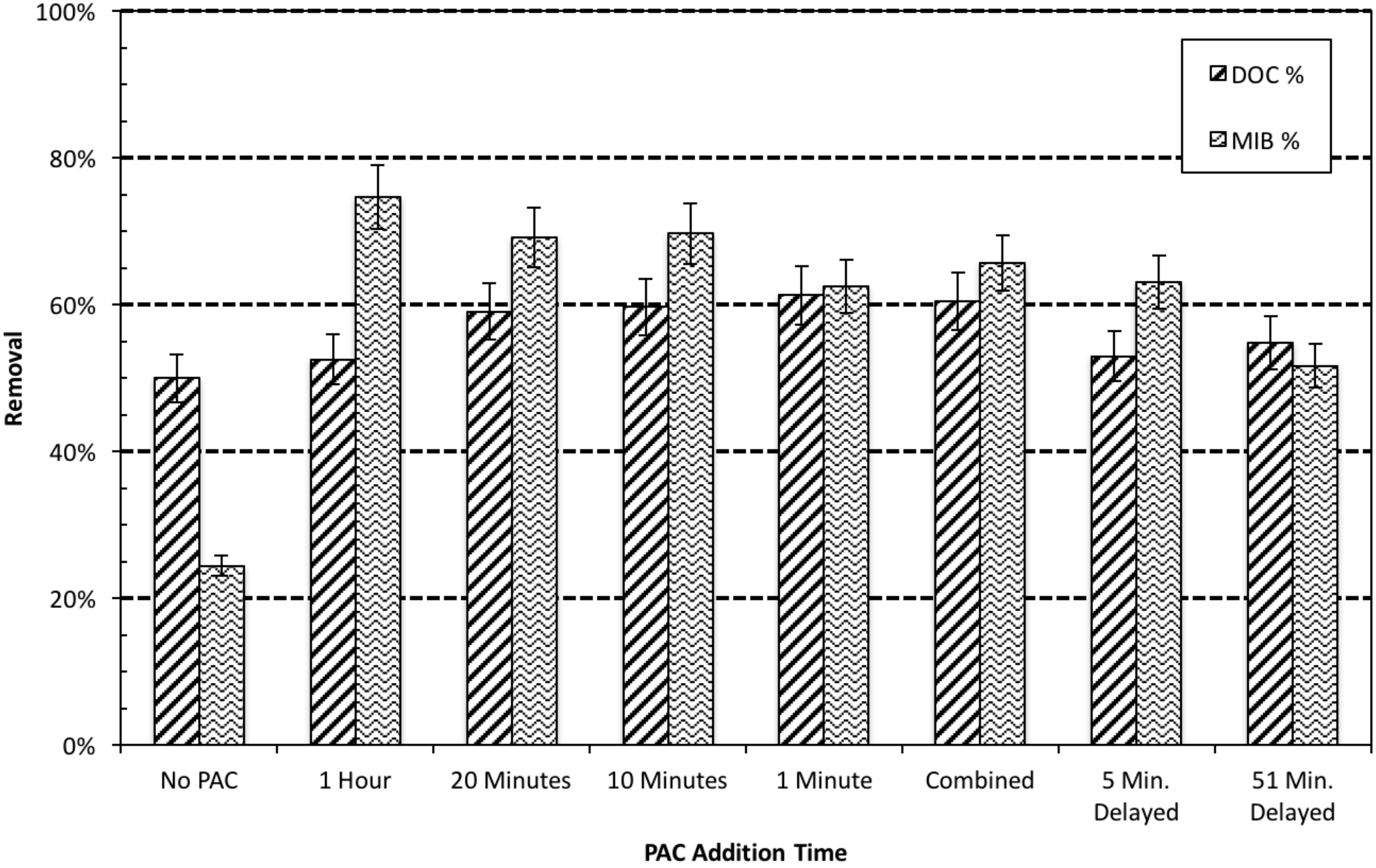

Figure 6.3: DOC and MIB removals for FCB with seven different PAC addition points and control (no PAC); 30 mg/L PAC; 40 mg/L alum.

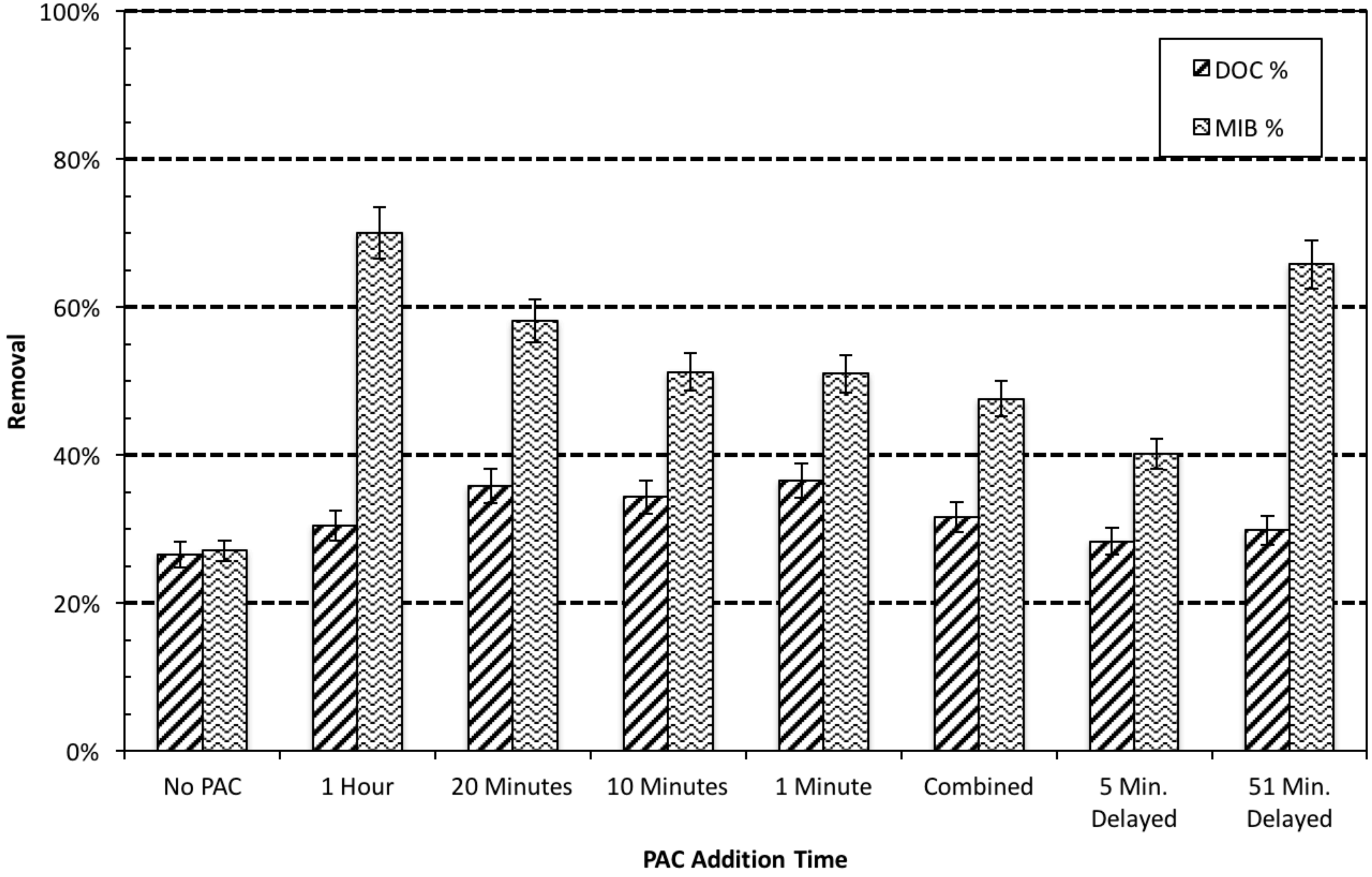

Figure 6.4: DOC and MIB removals for GLR with seven different PAC addition points and control (no PAC); 30 mg/L PAC; 40 mg/L alum.

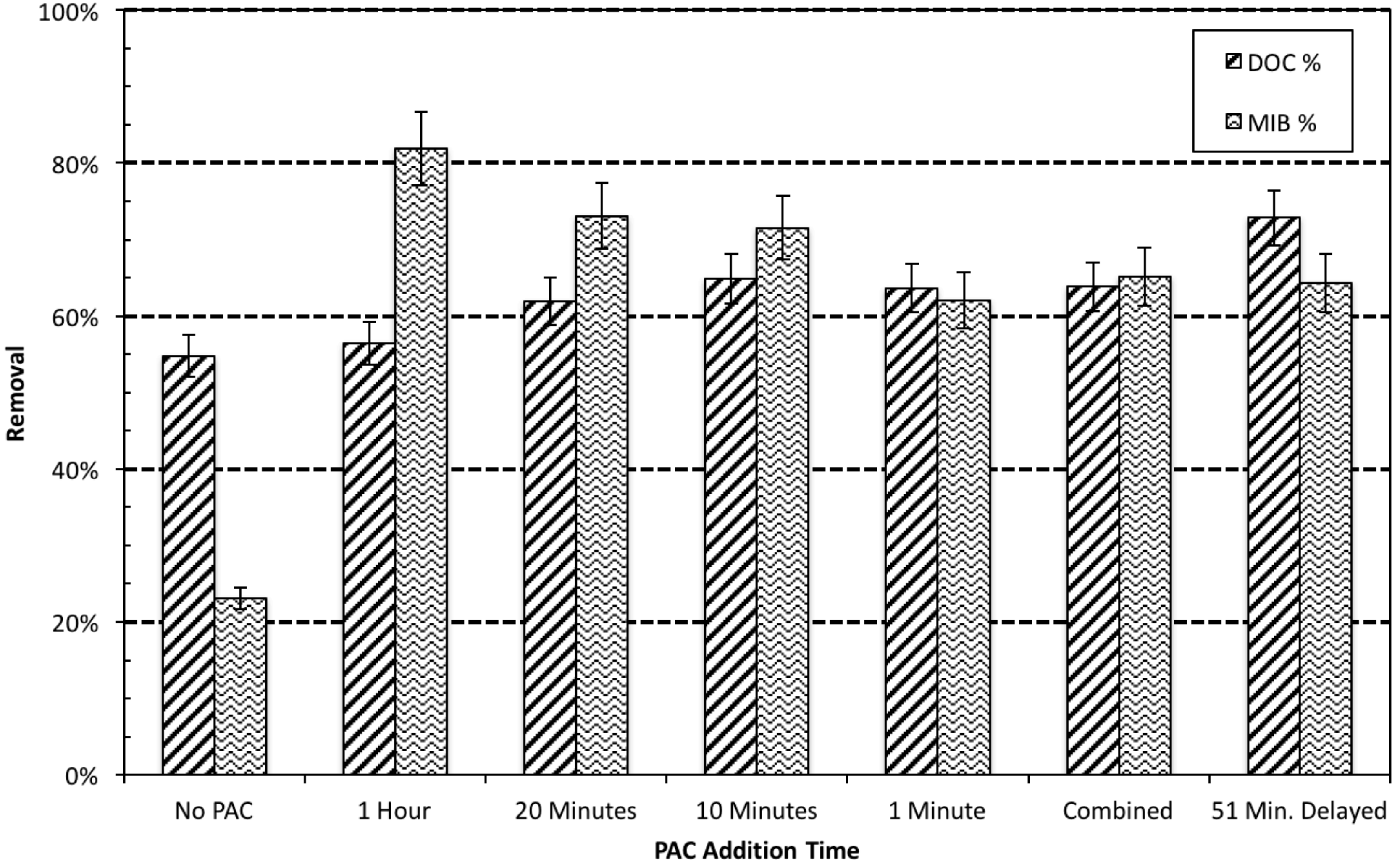

Figure 6.5: DOC and MIB removals for BC2 with seven different PAC addition points and control (no PAC); 30 mg/L PAC; 40 mg/L alum.

6.3.4. Molecular Size Fraction Influence

Two distinct MS fractions were fractionated from a surface water in Colorado (Big Elks Meadow, BEM). The large size fraction is >1kDa, while the small fraction is <1kDa. The water quality parameters for these two waters are presented in Table 6.1. These size fractions were evaluated for their contribution to adsorption competition with MIB. Experiments with three waters were performed similarly to the PAC pre-treatment; however, in these tests, only two pre-treatment contact times were evaluated. One minute and ten minutes of contact prior to coagulation were evaluated as earlier results demonstrated the benefit of ten minutes over longer contact times and the need for pre-treatment with PAC. Five minutes delayed addition was also evaluated to provide a reference point to the previous research. Mixing both the large and small MS fractions into a blend of equal parts on a mass basis resulted in a DOC of 6.5 mg-C/L and was tested under these conditions. Figure 6.6 and Figure 6.7 present the removal of both DOC and MIB for the small (<1kDa) and large (>1kDa) MS fractions at and alum dose of 40 mg/L and a PAC dose of 30 mg/L. For these tests, the small MS fraction had an initial DOC of 5.7 mg-C/L and MIB of 565 ng/L; the large size fraction had an initial DOC of 7.5 mg-C/L and 575 ng/L of MIB. Figure 6.8 shows DOC and MIB removal for a mixture of equal parts, on a mass of DOC basis, both the large and small MS fractions at an initial DOC of 6.3 mg-C/L and 451 ng/L of MIB. For the small MS fraction alone, shown in Figure 6.6, delayed PAC addition provided more MIB removal than did the other addition points. For this MS fraction, more of the strongly adsorbing, or directly competing, organic molecules are removed by coagulation. The background water matrix had a SUVA value of 1.8 $\text{mg*L}^{--1}\text{*m}^{-1}$, which is in the low range, indicating that it is less reactive and harder to coagulate, however, there was still near 40% removal of DOC in all cases. The final SUVA was also 1.8 mg*L^{-1}*m^{-1}. However, coagulation did not only remove the aromatic, strongly absorbing fraction as indicated by no change in SUVA value. Conversely, when the larger MS fraction was coagulated, the SUVA dropped from 2.4 to 1.7 mg*L^{-1}*m^{-1}. This type of sharp drop is expected from coagulation (Weishaar, et al., 2003) when the larger, more aromatic molecules are easier to coagulate.

The large MS fraction, shown in Figure 6.7, resulted in more removal than was observed in the small MS fraction, for both DOC and MIB. This is to be expected based on the mechanisms and interferences of MIB adsorption. The large MS fraction water had a higher SUVA, suggesting that coagulation will be more effective. The smaller MS fraction is more competitive with MIB as demonstrated by more MIB removal observed in the large size fraction. After coagulation, which tends to remove larger molecules, smaller molecules remain, well above the 300 Dalton range of strong competition (Hepplewhite, et al., 2004).

Figure 6.8 shows the mixture of large and small size fractions. MIB and DOC removals were averaged between the two discrete MS fraction tests and then compared to those observed in the mixture test. Table 6.2 shows the percent difference between the average MIB and DOC removals observed in the MS fraction tests and the mixture test. Little difference was found, indicating that the competitive effect of the two MS fractions is additive because the average results are close to the mixture. The differences shown in Table 6.2 are within the level of error discussed in section 6.2.9.

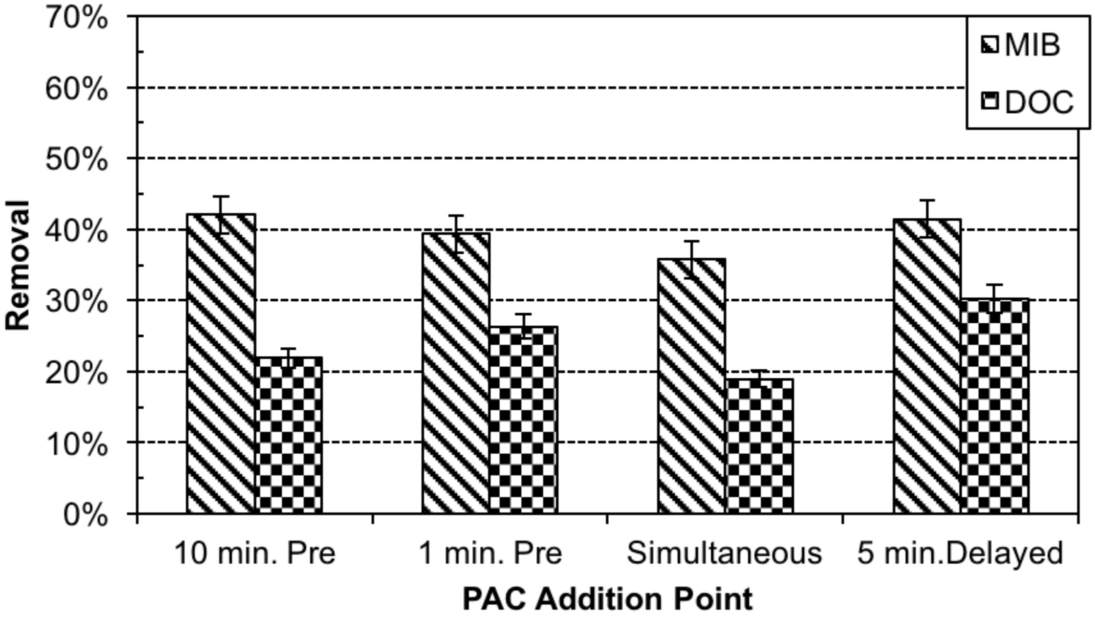

Figure 6.6: MIB and DOC removal for the small MS fraction at different PAC addition points. Initial DOC of 5.7 mg-C/L and MIB of 565 ng/L. PAC dose of 30 mg/L and alum dose of 40 mg/L.

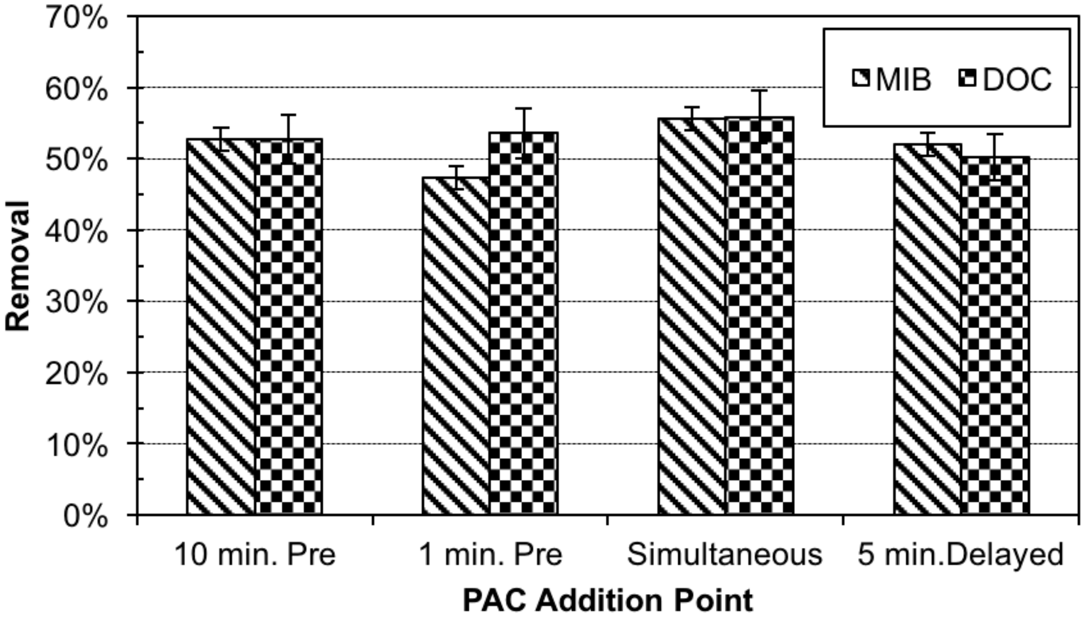

Figure 6.7: MIB and DOC removal for the large MS fraction at different PAC addition points. Initial DOC of 7.5 mg-C/L and MIB of 575 ng/L. PAC dose of 30 mg/L and alum dose of 40 mg/L.

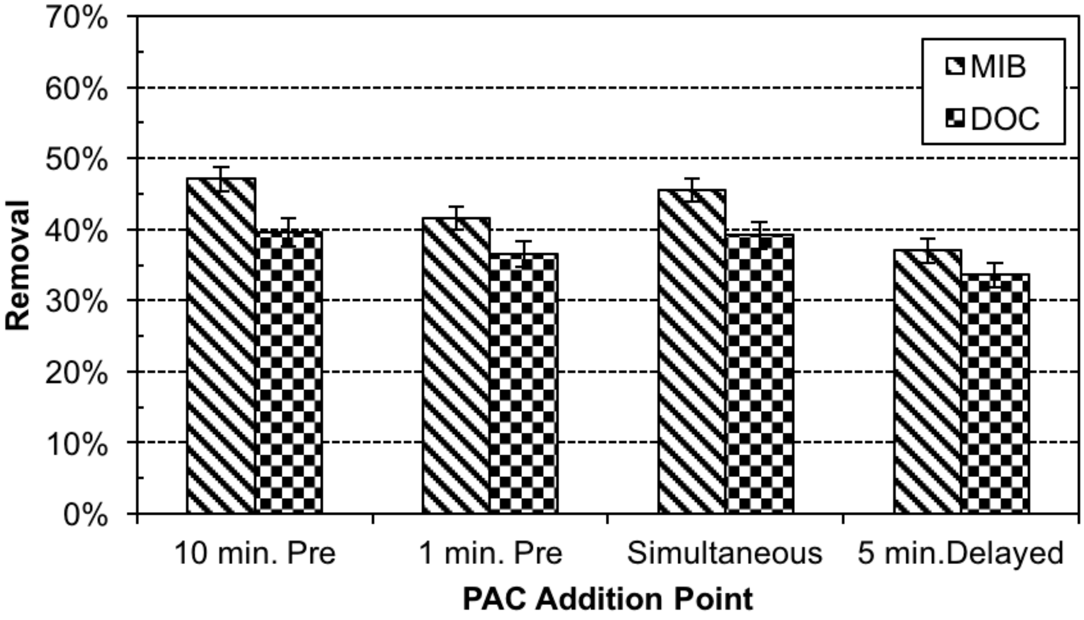

Figure 6.8: MIB and DOC removal for the blended DOM at different PAC addition points. Blend of equal contributions on a mass basis of both size fractions. Initial DOC of 6.3 mg-C/L and 451 ng/L of MIB.

Table 6.2: Difference between average MIB and DOC removals of the two MS fraction tests and the mixture test. The average difference for both DOC and MIB is less than 5%.

Addition Point	MIB	DOC
10 min. Pre	1%	3%
1 min. Pre	2%	3%
Simultaneous	0%	2%
5 min. Delayed	10%	7%
Average Difference	**3%**	**4%**

6.3.5. Wastewater PAC Addition

Exploring the impact of staged treatment in a different background matrix, such as wastewater, may help to provide insight into the use of PAC for a range of waters.

Figure 6.9 shows MIB and DOC removals with varied PAC addition in wastewater effluent (source: City of Boulder Wastewater Treatment Plant). The use of PAC increased DOM removal in all cases and five-minute delayed addition showed the best DOC removal. Simultaneous addition of PAC showed the best MIB removal. In this case, DOM that was removed by coagulation was the strongly competing fraction as indicated by pretreatment having lower MIB removal.

These results are consistent with previous studies (Shimabuku, et al. 2014) which showed that waters with higher FI values have more competition of DOM with MIB adsorption. This wastewater effluent had an influent FI of 1.88, the highest evaluated in this study. Based on these results, it appears as if PAC is effective in this wastewater and the most effective if it is used simultaneously with coagulants as both DOC and MIB removal are over 40%. The previously determined ten-minute pre-treatment with PAC was not the best option for wastewater effluent due to the exceptionally high influent FI of 1.88.

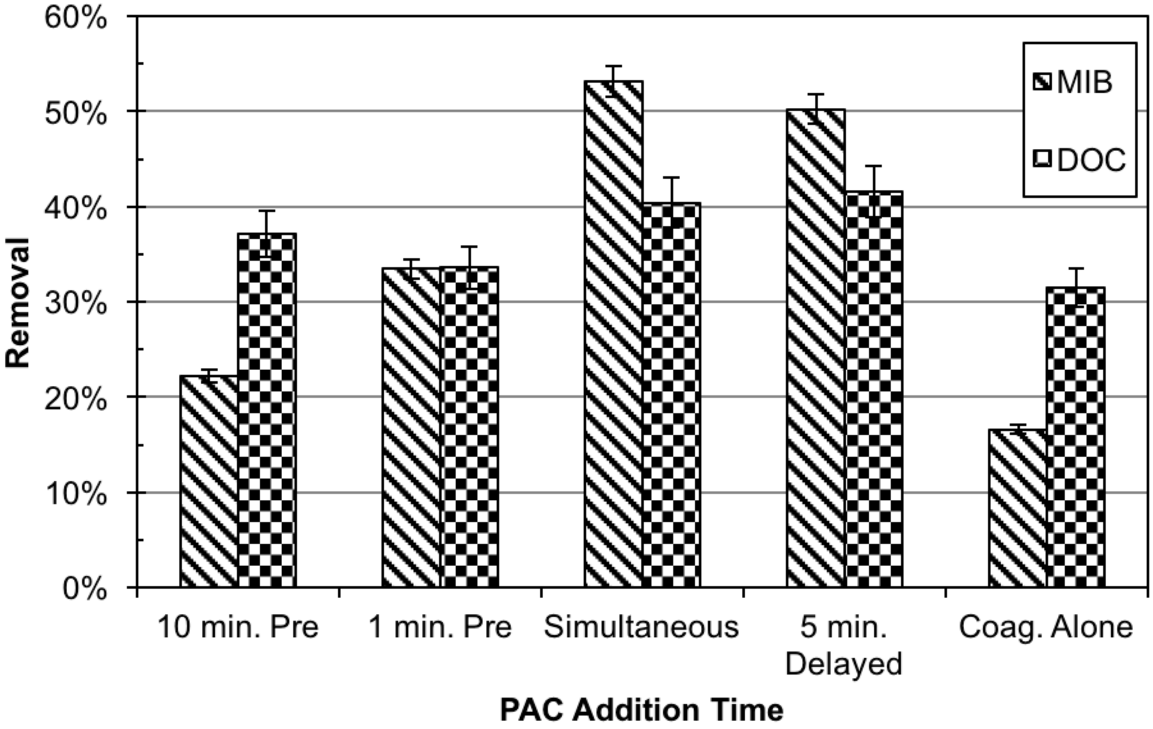

Figure 6.9: MIB and DOC removal for the wastewater sample at different PAC addition points. PAC does of 30 mg/L, alum dose of 80 mg/L

6.3.6. Indicator Parameters

Fluorescence was examined to determine if the FI could be used as an indicator of MIB removal. Figure 6.10 displays influent FI values against MIB removal through a ten minute addition point of PAC prior to coagulation. These results are consistent with previous research that found that FI could be used as an indicator for the competitive nature of organic matter with MIB (Shimabuku, et al., 2014). If water is pre-treated with PAC prior to coagulation, FI is a sufficient indicator of how much MIB will relatively be removed. MIB removal at the other addition locations were plotted against FI and fit with a power function. For the simultaneous addition location, the wastewater sample was omitted to demonstrate the ability of this correlation in surface water supplies. Table 6.3 shows how other influent FI and MIB removal are correlated when alternate

PAC addition locations are examined. The other addition times showed substantial correlations with the exception of the five-minute delayed test. This is because the FI relationship with the competing fraction of organic matter was established in absence of coagulants.

Table 6.3: Relationship between FI (x) and MIB removal (y). R^2 values for the four different PAC addition locations.

Addition Point	R^2	n	Regression Equation
10 min Pre	0.91	6	$y=17e^{-2.3x}$
1 min Pre	0.74	6	$y=3e^{-1.2x}$
Simultaneous	0.87	5	$y=3e^{-4.5x}$
5 min Delay	0.15	6	$y=0.7e^{-0.7x}$

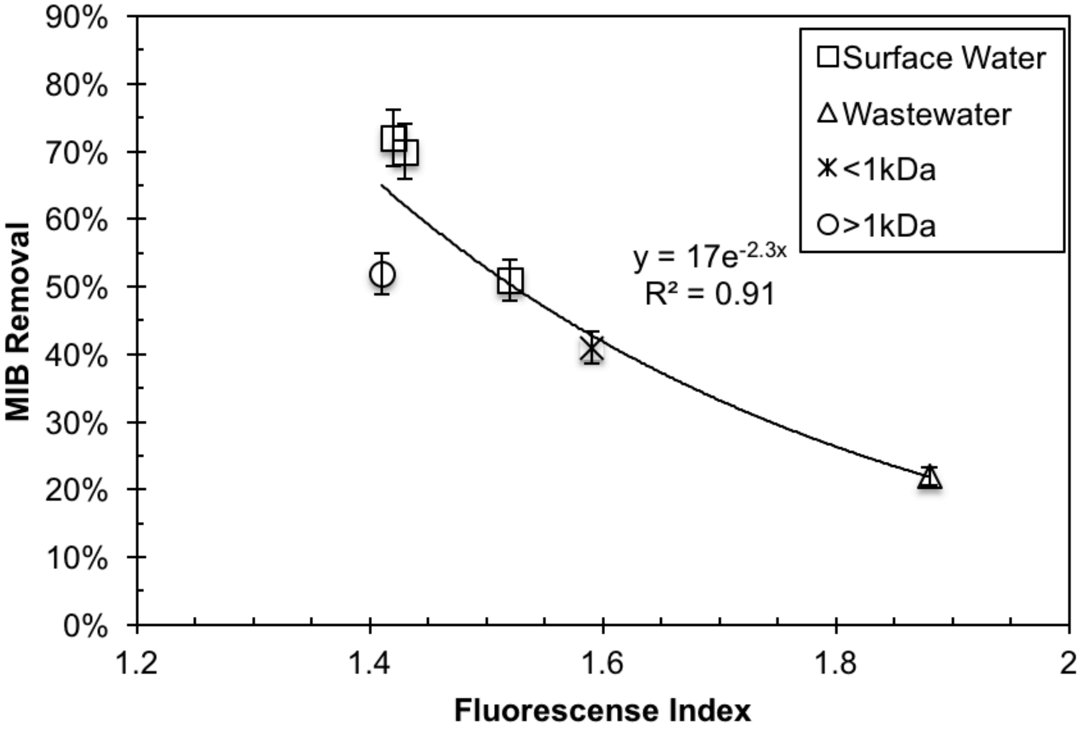

Figure 6.10: FI as an indicator of MIB removal for three surface waters, one wastewater effluent, and two DOM MS fractions. Results are for the ten-minute PAC contact time prior to coagulation.

6.4 Summary & Conclusion

The point of PAC addition was evaluated for three surface waters, one wastewater, and two MS fractions. It was found that for the surface waters ten minutes prior to coagulation was the best location to add PAC to remove MIB. While the one-hour contact time provided better removal of MIB the large size requirements for a one-hour contact time for large surface water treatment plants. Delaying the addition of PAC after coagulation for MIB removal did not yield enhanced removal of MIB. The size fraction remaining was the more competitive size fraction as indicated by the MS fraction tests.

Investigation of the two MS fractions and a blend of equal parts provided insight as to what the interferences are in the pre-treatment process. The MS fractions helped explain that coagulation removes the fraction of organic matter that does not compete for PAC adsorption with MIB. The smaller MS fraction is known to be the more strongly competing fraction. In the tests with the small MS fraction the lowest removal of MIB was observed. MIB removal in the larger MS fraction was nearly double that in the small MS fraction, supporting that the small MS fraction competes to a greater extent. This means that when coagulants are used to remove large DOM molecules, the DOM remaining is smaller and strongly competitive in nature with MIB for sites on PAC. When the removals of both MS fractions were averaged together and compared to the blend, there was minimal difference, within 5% on average. PAC removal of MIB and DOC in wastewater was also evaluated and it was found that the use of PAC helps to remove bulk DOC, as well as performs well (~50% removal) at reducing influent MIB concentrations. However, unlike other waters examined in this study, adding PAC ten minutes before coagulation yielded the worst performance, and 5 minutes delayed or simultaneous addition was the best when targeting MIB, as coagulation removes a large portion of the competing MS fraction from wastewater.

These findings shed light on the current practice of adding PAC simultaneously with the coagulant based on three surface waters, on average an additional 18 and 12 percent removal of MIB in surface waters could be achieved with the addition of PAC 1 hour and 10 min prior to coagulation, respectively. If there is an equalization basin, storage tank, or long (>10 minutes) influent pipeline to a drinking water treatment plant, then adding PAC seasonally at this location instead of the rapid mix may be desirable.

Chapter 7
Summary & Recommendations

7.1 Summary

The work presented in Chapter 5 evaluated kinetics of DOM coagulation and the impact on conventional drinking water treatment. Eight waters with a range of water quality were evaluated. Four water quality parameters (pH, turbidity, temperature, and molecular size) and three operational parameters (mixing speed, coagulant type, and coagulant dose) were varied to assess their impact on DOM coagulation kinetics. It was found that under all cases examined after 30 seconds of rapid mix, DOC reaches equilibrium and no further removal is seen.

Based on these results, PAC addition, chlorine disinfection, and direct filtration were evaluated to determine if the time-scale of coagulation has an impact on the processes. For PAC addition, delaying PAC input by five and fifty-one minutes was investigated and did not present conclusive evidence as to where the best point within a coagulation process is to add PAC. For MIB removal, delayed addition almost always resulted in decreased efficiency for adsorption. These results support the concept that coagulation does not remove the competing fraction of organic matter, instead, organic molecules that are strongly sorbable remain.

DBP yields were calculated after chlorine was added to a system simultaneously with alum and one minute after alum coagulation. These results indicate that chlorine could be applied short after coagulant addition to provide a higher CT. TTHM data of both the chlorine addition locations were not substantially different, but HAA5 concentrations were lower in the delayed chlorine addition case.

Direct filtration was inherently examined in all coagulation experiments. Once water was sampled, it was directly and promptly filtered through a 0.45-micron membrane filter. This is representative of a direct filtration system where process water is not provided long contact times with flocs and does not undergo extensive flocculation. These results display that when DOC, i.e., DBP precursors, are the main contaminant of concern direct filtration is desirable.

Research in Chapter 6 examined various locations of PAC addition around the coagulation process. Pre-addition, simultaneous addition, and delayed addition relative to coagulant addition were evaluated for MIB and DOC removals. Coagulation removed the competing contaminant, DOM within 30 seconds, so competition should be marginalized after coagulation; however, this was not the case. Results clearly demonstrate that there is not a clear optimal addition point between simultaneous and delayed addition, contrary to previous thought. Instead, PAC worked best at removing MIB in absence of coagulation, leading to further exploration of pre-addition with PAC.

Four different pre-PAC addition times were evaluated, one, ten, twenty, and sixty minutes, as well as simultaneous and delayed addition of 51 minutes, all relative to the addition of the coagulant. It was found that additional removal of DOC occurred in all cases and MIB removal was higher during earlier addition times or longer contact times. A pre-addition contact time of ten minutes was selected as the “best” point of addition to control both DOC and MIB. Results did not show significant difference between ten and twenty minutes of contact prior to coagulation, but longer contact times require higher costs and more space for system operation.

FI was examined as an indicator for MIB removal through the ten-minute pre-addition process. It was found that FI was an indicator of the overall MIB removal through this process and FI has been previously shown to be a good indicator for the competitive nature of organic matter. Organic matter is the main competing constituent with MIB.

7.2 Recommendations

The findings highlight the need to closely investigate coagulation of DOM on a kinetic basis. Traditional practice, based on particle removal, is to allow enough time for flocs to grow until they can settle readily in a sedimentation tank. However, the bulk DOC reaches equilibrium with the flocs in 30 seconds, causing additional flocculation to be less vital for DOC removal than previously thought. Because the DOM is complexed in the floc structure this quickly, chlorine addition immediately after coagulation may be a viable option.

Based on these findings, it is suggested that utilities using PAC add it prior to the rapid mix process. While the attractiveness of adding PAC during the rapid mix is apparent because there is already a system in place to provide substantial mixing, additional MIB removal that may be achieved by a pre-addition of PAC is beneficial. Addition in the influent pipeline or in an equalization basin would each provide enhanced contact time for PAC prior to coagulation. Addition in an influent pipeline would be more cost effective as there is no need for major additional capital improvements.

Chapter 8
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Appendix

Chapter 5 Source Information

Figure 5.1 and 5.2 source information:

Water: BC1 **Date Rec'd:** May-2014 **Test Date:** Jun-2014

Variable Coag Dose

Raw Water Characteristics		0	20	40	80	160
pH, T (C)	6.94	6.93	6.72	6.17	4.71	4.44
UVA (cm^{-1})	0.166	0.146	0.056	0.030	0.024	0.037
Turbidity (NTU)	7.5	3.67	1.28	0.752	5.88	7.6
TOC (mg/L)	5.39	5.13	3.24	2.14	2.22	2.815
Alkalinity (mg/L)	18					

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Feb-2014

Variable Coag Dose

Raw Water Characteristics		0	20	40	80	160	80 (dup)
pH, T (C)	7.69	7.67	7.39	7.14	6.34	4.47	6.12
UVA (cm^{-1})	0.211	0.204	0.144	0.089	0.054	0.056	0.053
Turbidity (NTU)	36.5	28.9	34.1	4.43	2.34	3.62	1.97
TOC (mg/L)	7.5	7.81	6.46	4.78	3.55	3.21	3.45
Alkalinity (mg/L)	35						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Apr-2014

Variable Coag Dose

Raw Water Characteristics		0	20	40	80	160	40 (dup)
pH, T (C)	7.4	7.36	6.7	6.34	5.53	4.64	6.12
UVA (cm^{-1})	0.107	0.104	0.052	0.031	0.02	0.03	0.027
Turbidity (NTU)	11.3	6.93	1.89	1.69	2	2.81	1.4
TOC (mg/L)	4.4	4.86	3.2	2.46	2.26	2.41	2.48
Alkalinity (mg/L)	25						

Water: DW4 **Date Rec'd:** Sep-2014 **Test Date:** Sep-2014

Variable Coag Dose

Raw Water Characteristics		0	20	40	80	160
pH, T (C)	7.3	7.16	6.33	6.05	5.00	4.41
UVA (cm^{-1})	0.109	0.109	0.046	0.027	0.025	0.033
Turbidity (NTU)	5.5	3.48	0.55	0.46	2.67	3.95
TOC (mg/L)	4	4.015	2.5	1.885	1.635	2.105
Alkalinity (mg/L)	30					

Figure 5.3a and 5.3b source information:

Water: BC2 **Date Rec'd:** Jul-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**0.25**	**0.5**	**1**	**5**	**10**
pH, T (C)	7.2						
UVA (cm^{-1})	0.072						
Turbidity (NTU)	3.1						
TOC (mg/L)	2.3	2.16	0.92	0.98	0.94	0.98	1.06
Alkalinity (mg/L)	24						

Water: CUP **Date Rec'd:** Jul-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**0.25**	**0.5**	**0.75**	**5**	**10**
pH, T (C)	7.3						
UVA (cm^{-1})	0.097						
Turbidity (NTU)	15.6						
TOC (mg/L)	3.2	3.15	1.71	1.71	1.71	1.77	1.96
Alkalinity (mg/L)	30						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**0.25**	**0.5**	**0.75**	**5**	**10**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.40	2.53	1.98	2.00	2.23	2.14
Alkalinity (mg/L)	25						

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**0.25**	**0.5**	**0.75**	**5**	**10**
pH, T (C)	7.5						
UVA (cm^{-1})	0.105						
Turbidity (NTU)	6.2						
TOC (mg/L)	3.8	3.78	1.96	1.96	2.01	2.06	2.18
Alkalinity (mg/L)	35						

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**0.25**	**0.5**	**1**	**5**	**10**
pH, T (C)	8.6						
UVA (cm^{-1})	0.124						
Turbidity (NTU)	3.5						
TOC (mg/L)	8.0	7.33	5.48	5.89	5.69	5.33	5.84
Alkalinity (mg/L)	128						

Figure 5.4 source information:

Water: BC2 **Date Rec'd:** Jul-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.2						
UVA (cm^{-1})	0.072						
Turbidity (NTU)	3.1						
TOC (mg/L)	2.3	2.30	0.89	0.92	0.95	0.90	0.99
Alkalinity (mg/L)	24						

Water: CUP **Date Rec'd:** Jul-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.3						
UVA (cm^{-1})	0.097						
Turbidity (NTU)	15.6						
TOC (mg/L)	3.2	3.23	1.46	1.48	1.42	1.55	1.46
Alkalinity (mg/L)	30						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Jun-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.31	2.57	2.2	2.41	2.38	2.53
Alkalinity (mg/L)	25						

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Jun-2014

Variable: Time (min)

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.5						
UVA (cm^{-1})	0.105						
Turbidity (NTU)	6.2						
TOC (mg/L)	3.8	3.87	2.01	2.19	2.07	2.13	2.00
Alkalinity (mg/L)	35						

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Jul-2014

Variable: Time (min)

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	8.6						
UVA (cm^{-1})	0.124						
Turbidity (NTU)	3.5						
TOC (mg/L)	8.0	7.95	6.27	5.79	5.87	6.16	6.01
Alkalinity (mg/L)	128						

Water: BC1 **Date Rec'd:** May-2014 **Test Date:** Jun-2014

Variable: Time (min)

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	6.94						
UVA (cm^{-1})	0.166						
Turbidity (NTU)	7.5						
TOC (mg/L)	5.39	5.00	2.45	2.06	2.33	2.39	2.68
Alkalinity (mg/L)	18						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jun-2014

Variable: Time (min)

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.06	3.76	3.47	3.48	3.81	3.92
Alkalinity (mg/L)	35						

Water: B.Res **Date Rec'd:** Jun-2014 **Test Date:** Jun-2014

Variable: Time (min)

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	8.5						
UVA (cm^{-1})	0.088						
Turbidity (NTU)	2.8						
TOC (mg/L)	4.7	4.71	3.35	3.27	3.26	3.3	3.34
Alkalinity (mg/L)	114						

Figure 5.5 source information:

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jun-2014
Variable: Time (min) Baseline

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.8	3.5	3.5	3.8	3.9
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014
Variable: Time (min) Mixing Speed: 55 rpm

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	4.0	4.0	4.0	4.1	4.1
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014
Variable: Time (min) Mixing Speed: 125 rpm

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.8	4.0	4.0	4.1	4.2
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014
Variable: Time (min) Temperature: 10 ºC

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.9	3.8	3.9	3.9	4.1
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014

Variable: Time (min) Temperature: 30 ºC

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	4.2	4.2	4.3	4.5	4.6
Alkalinity (mg/L)	35						

Figure 5.6 source information:

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jun-2014

Variable: Time (min) Baseline

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.8	3.5	3.5	3.8	3.9
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014

Variable: Time (min) Turbidity: 20 NTU

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.9	4.1	4.7	4.2	4.3
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014

Variable: Time (min) Turbidity: 80 NTU

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	4.4	4.1	4.2	4.4	4.6
Alkalinity (mg/L)	35						

Figure 5.7 source information:

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jun-2014

Variable: Time (min) Baseline

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.8	3.5	3.5	3.8	3.9
Alkalinity (mg/L)	35						

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Aug-2014

Variable: Time (min) Coagulant: Ferric Chloride

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.1	3.9	3.9	4.0	4.1	4.1
Alkalinity (mg/L)	35						

Figure 5.8 source Information

Water: B.Res **Date Rec'd:** Jun-2014 **Test Date:** Aug-2014

Variable: Time (min) pH: ambient

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.5						
UVA (cm^{-1})	0.088						
Turbidity (NTU)	2.8						
TOC (mg/L)	4.7	4.71	3.35	3.27	3.26	3.3	3.34
Alkalinity (mg/L)	114						

Water: B.Res **Date Rec'd:** Jun-2014 **Test Date:** Aug-2014

Variable: Time (min) pH: 7

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.5						
UVA (cm^{-1})	0.088						
Turbidity (NTU)	2.8						
TOC (mg/L)	4.7	4.71	2.99	2.97		3.09	3.13
Alkalinity (mg/L)	114						

Water: B.Res **Date Rec'd:** Jun-2014 **Test Date:** Aug-2014

Variable: Time (min) pH: 7.5

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.5						
UVA (cm^{-1})	0.088						
Turbidity (NTU)	2.8						
TOC (mg/L)	4.7	4.71	3.19	3.15	3.22	3.22	3.23
Alkalinity (mg/L)	114						

Figure 5.9 source information

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Aug-2014

Variable: Time (min) Coag Dose: 10 mg/L

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.4	3.5	3.6	3.5	3.7	3.7
Alkalinity (mg/L)	25						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Aug-2014

Variable: Time (min) Coag Dose: 20 mg/L

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.4	2.6	2.6	2.7	2.7	2.8
Alkalinity (mg/L)	25						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Aug-2014

Variable: Time (min) Coag Dose: 30 mg/L

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.4	2.3	2.2	2.3	2.4	2.4
Alkalinity (mg/L)	25						

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Aug-2014

Variable: Time (min) Coag Dose: 40 mg/L

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.4	2.57	2.2	2.41	2.38	2.53
Alkalinity (mg/L)	25						

Figure 5.10 source information

Water: >1K **Date Rec'd:** Jun-2012 **Test Date:** Aug-2014

Variable: Time (min)

Raw Water Characteristics		0	0.5	1	20	51
pH, T (C)	7.6					
UVA (cm^{-1})	0.169					
TOC (mg/L)	6.5	6.49	3.38	3.45	3.7	3.81

Water: <1K **Date Rec'd:** Jun-2012 **Test Date:** Aug-2014

Variable: Time (min)

Raw Water Characteristics		0	0.5	1	20	51
pH, T (C)	7.4					
UVA (cm^{-1})	0.116					
TOC (mg/L)	6.5	6.34	4.6	4.42	4.89	5.27

Figure 5.11 source information:

Water: BWW-Effluent **Date Rec'd:** Sep-2012 **Test Date:** Oct-2014
Variable: Time (min)

Raw Water Characteristics		**0**	**0.5**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.1							
TOC (mg/L)	6.8	6.8	5.85	5.76	5.20	5.70	5.81	5.35

Water: BWW-Influent **Date Rec'd:** Sep-2012 **Test Date:** Oct-2014
Variable: Time (min)

Raw Water Characteristics		**0**	**0.5**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.5							
TOC (mg/L)	23	23	22.7	23.1	23	22.8	22.8	23.7

Figure 5.12 and 5.13 source information

Water: BC1 **Date Rec'd:** May-2014 **Test Date:** Jul-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		**1 min PAC**	**PAC Final**	**Comb. Final**	**Coag 5 min PAC**	**Coag 51 min PAC**	**Coag Alone**
pH, T (C)	6.9						
UVA (cm^{-1})	0.166						
Turbidity (NTU)	7.5						
TOC (mg/L)	5.39	4.97	4.23	1.65	1.6	1.84	2.22
MIB (ng/L)	187	126	76	106	105	83	178

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jul-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		**1 min PAC**	**PAC Final**	**Comb. Final**	**Coag 5 min PAC**	**Coag 51 min PAC**	**Coag Alone**
pH, T (C)	7.7						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	6.37	6.51	3.82	4.00	3.76	4.00
MIB (ng/L)	175	121	85	116	96	78	178

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Jul-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		1 min PAC	PAC Final	Comb. Final	Coag 5 min PAC	Coag 51 min PAC	Coag Alone
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.40	3.64	1.94	2.14	1.85	2.26
MIB (ng/L)	193	152	78	99	109	86	190

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Jul-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		1 min PAC	PAC Final	Comb. Final	Coag 5 min PAC	Coag 51 min PAC	Coag Alone
pH, T (C)	7.5						
UVA (cm^{-1})	0.105						
Turbidity (NTU)	6.2						
TOC (mg/L)	3.8	3.56	3.20	1.55	1.80	1.73	2.00
MIB (ng/L)	173	126	66	88	64	90	171

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Jul-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		1 min PAC	PAC Final	Comb. Final	Coag 5 min PAC	Coag 51 min PAC	Coag Alone
pH, T (C)	8.6						
UVA (cm^{-1})	0.124						
Turbidity (NTU)	3.5						
TOC (mg/L)	8.0	7.34	6.69	5.72	5.7	5.58	6.01
MIB (ng/L)	185	145	112	13	110	121	156

Chapter 6 Source Information

Figure 6.1 source information:

Water: BC1 **Date Rec'd:** May-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	6.94						
UVA (cm^{-1})	0.166						
Turbidity (NTU)	7.5						
TOC (mg/L)	5.39	5	4.65	3.94	3.87	3.91	3.77

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.69						
UVA (cm^{-1})	0.211						
Turbidity (NTU)	36.5						
TOC (mg/L)	7.5	7.06	6.25	5.82	5.57	5.54	4.94

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.4						
UVA (cm^{-1})	0.107						
Turbidity (NTU)	11.3						
TOC (mg/L)	4.4	4.31	3.74	3.05	2.99	2.84	2.85

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		0	1	5	10	20	51
pH, T (C)	7.5						
UVA (cm^{-1})	0.105						
Turbidity (NTU)	6.2						
TOC (mg/L)	3.8	3.87	3.56	3.38	3.41	3.47	3.2

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**0**	**1**	**5**	**10**	**20**	**51**
pH, T (C)	8.6						
UVA (cm^{-1})	0.124						
Turbidity (NTU)	3.5						
TOC (mg/L)	8.0	7.95	7.34	7.46	7.29	7.09	6.69

Figure 6.2 source information:

Water: BC1 **Date Rec'd:** May-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**1**	**51**
pH, T (C)	6.94	126	76
UVA (cm^{-1})	0.166		
MIB (ng/L)	187		
TOC (mg/L)	5.39		

Water: DW2 **Date Rec'd:** Dec-2013 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**1**	**51**
pH, T (C)	7.69	121	85
UVA (cm^{-1})	0.211		
MIB (ng/L)	175		
TOC (mg/L)	7.5		

Water: DW3 **Date Rec'd:** Apr-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**1**	**51**
pH, T (C)	7.4	152	78
UVA (cm^{-1})	0.107		
MIB (ng/L)	193		
TOC (mg/L)	4.4		

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**1**	**51**
pH, T (C)	7.5	126	66
UVA (cm^{-1})	0.105		
MIB (ng/L)	173		
TOC (mg/L)	3.8		

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Jul-2014

Variable: time (min) PAC: 30 mg/L

Raw Water Characteristics		**1**	**51**
pH, T (C)	185		
UVA (cm^{-1})	0.124		
MIB (ng/L)	185	145	112
TOC (mg/L)	8.0		

Figure 6.3, Figure 6.4, and Figure 6.5 source information:

Water: BC2 **Date Rec'd:** May-2014 **Test Date:** Aug-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		No PAC	1 Hour	20 Minutes	10 Minutes	1 Minute	Combined	51 Min. Delayed
pH, T (C)	7.2							
UVA (cm^{-1})	0.072							
Turbidity (NTU)	3.1							
TOC (mg/L)	2.3	1.03	1.01	0.87	0.81	0.83	0.83	0.62
MIB (ng/L)	289	222	52	78	80	110	101	106

Water: FCB **Date Rec'd:** Sep-2014 **Test Date:** Aug-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		No PAC	1 Hour	20 Minutes	10 Minutes	1 Minute	Combined	5 Min. Delayed	51 Min. Delayed
pH, T (C)	7.5								
UVA (cm^{-1})	0.105								
Turbidity (NTU)	6.2								
TOC (mg/L)	3.8	1.87	1.77	1.56	1.53	1.47	1.53	1.77	1.73
MIB (ng/L)	657	497	166	202	199	247	226	244	315

Water: GLR **Date Rec'd:** Jun-2014 **Test Date:** Sep-2014

Variable: addition time PAC: 30 mg/L Coag: 40 mg/L

Raw Water Characteristics		No PAC	1 Hour	20 Minutes	10 Minutes	1 Minute	Combined	5 Min. Delayed	51 Min. Delayed
pH, T (C)	8.6								
UVA (cm^{-1})	0.124								
Turbidity (NTU)	3.5								
TOC (mg/L)	8.0	5.85	5.61	5.13	5.27	5.02	5.42	5.75	5.63
MIB (ng/L)	1049	770	315	437	512	509	548	625	354

Figure 6.6, Figure 6.7, and Figure 6.8 source information:

Water: >1K **Date Rec'd:** Jun-2012 **Test Date:** Sep-2014

Variable: Time (min)

Raw Water Characteristics		**10 min Pre**	**1 min Pre**	**Simultaneous**	**5 min. delayed**
pH, T (C)	7.6				
UVA (cm^{-1})	0.169				
TOC (mg/L)	7.5	3.52	3.46	3.29	3.72
MIB (ng/L)	575	272	303	255	277

Water: <1K **Date Rec'd:** Jun-2012 **Test Date:** Sep-2014

Variable: Time (min)

Raw Water Characteristics		**10 min Pre**	**1 min Pre**	**Simultaneous**	**5 min. delayed**
pH, T (C)	7.4				
UVA (cm^{-1})	0.116				
TOC (mg/L)	5.69	4.52	4.19	4.61	3.99
MIB (ng/L)	565	327	342	363	334

Water: Blend **Date Rec'd:** Jun-2012 **Test Date:** Sep-2014

Variable: Time (min)

Raw Water Characteristics		**10 min Pre**	**1 min Pre**	**Simultaneous**	**5 min. delayed**
pH, T (C)	7.4				
UVA (cm^{-1})	0.116				
TOC (mg/L)	6.3	3.77	3.70	3.84	4.15
MIB (ng/L)	451	241	263	243	283

Figure 6.9 source information

Water: BWW **Date Rec'd:** Sep-2014 **Test Date:** Oct-2014

Variable: addition time PAC: 30 mg/L Coag: 80 mg/L

Raw Water Characteristics		**10 min. Pre**	**1 min. Pre**	**Simultaneous**	**5 min. Delayed**	**Coag. Alone**
pH, T (C)	8.1					
TOC (mg/L)	6.8	4.27	4.52	4.05	3.98	4.66
MIB (ng/L)	751	585	502	352	377	622

Figure 6.10 source information:

Source	**FI**	**10 min**	**1 min**	**Comb**	**5min D**
BWW	1.88	22%	33%	53%	50%
<1k	1.59	41%	39%	36%	41%
>1k	1.41	52%	47%	56%	52%
FCB	1.43	70%	62%	66%	63%
GLR	1.52	51%	51%	48%	40%
BC2	1.42	72%	62%	65%	64%